# the Acid Deposition Research Program

## BIOPHYSICAL RESEARCH

### THE PRESENT AND POTENTIAL EFFECTS OF ACIDIC AND ACIDIFYING AIR POLLUTANTS ON ALBERTA'S ENVIRONMENT

**CRITICAL POINT I**
**SUMMARY REPORT**

**A. H. Legge, Principal Investigator**

September, 1988

PRIME RESEARCH CONTRACTOR:
The Kananaskis Centre for Environmental Research
The University of Calgary
Calgary, Alberta, Canada

Acid Deposition Research Program

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# ALBERTA GOVERNMENT-INDUSTRY ACID DEPOSITION RESEARCH PROGRAM (ADRP)

# THE PRESENT AND POTENTIAL EFFECTS OF ACIDIC AND ACIDIFYING AIR POLLUTANTS ON ALBERTA'S ENVIRONMENT

## CRITICAL POINT I

## 1988

## SUMMARY REPORT

submitted
July 1988
by

The Kananaskis Centre for Environmental Research
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to the
Members Committee
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## FOREWORD

The Alberta Government/Industry Acid Deposition Research Program (ADRP) is jointly sponsored by the public and private sectors of Alberta. The Biophysics Research Program, which began in 1985, is a two-phase study designated by the terminal points **Critical Point I.** and **Critical Point II.** This document presents results to **Critical Point I.** and reports the culmination of three and one-half years of intensive study, including characterization of the background air quality of Alberta and determination of how this air quality is modified by emissions of oxides of sulphur and nitrogen within the Province. The measured air quality was integrated with modelling to evaluate present and potential regional-scale responses of selected environmental receptors.

Throughout the course of this Biophysics Research Program, advise, evaluation, and peer review has been provided on a regular basis by the members of a Science Advisory Board. The ten members of this board represent a total of approximately 170 years experience in the field of air pollution and its related environmental effects.

This ADRP Biophysics Research represents a holistic approach to the evaluation of the chemistry of multiphase atmospheric systems and their possible effects on the environment. While no environmental response studies per se were conducted in the field, this document identifies topics which require attention in the Alberta context.

In addition to the joint public/private sector sponsorship of the ADRP, the program to **Critical Point I.** was unique in that it was a "joint venture" project, primarily between The University of Calgary and the private sector. The research team was international in scope and included:

- Abboud, S.; Alberta Research Council, Terrain Science Department, Edmonton, Alberta: Project Leader, soil chemistry modelling.
- Bauman, S.; Element Analysis Corporation, Tallahassee, Florida: elemental analysis of particles.
- Colley, D.; Western Research, Calgary, Alberta: emissions inventory.
- Cooper, J.A.; Nuclear Element Analysis (NEA) Inc., Beaverton, Oregon: source apportionment.
- Crowther, R.; Aquatic Resource Management Ltd., Calgary, Alberta: water chemistry modelling.
- Davidson, C.; Carnegie Mellon University, Department of Civil Engineering, Pittsburgh, Pennsylvania: deposition velocity studies.
- Hansen, M.C.; Western Research, Calgary, Alberta: meteorology and air quality data management.
- Krouse, H.R.; University of Calgary, Physics Department, Calgary, Alberta: sulphur isotopes.
- Krug, E.C.; Illinois State Water Survey, University of Illinois, Champaign, Illinois: Project Leader, water chemistry modelling.
- Leahey, D.M.; Western Research, Calgary, Alberta: meteorology.
- Lefohn, A.S.; ASL and Associates, Helena, Montana: international air quality comparisons.
- Legge, A.H.; University of Calgary, Kananaskis Centre for Environmental Research, Calgary, Alberta: Principal Investigator, ADRP.
- Mathews, T.; University of Calgary, Department of Physics, Calgary, Alberta: atmospheric physics.

- McVehil, G.E.; McVehil-Monnet Associates, Englewood, Colorado; Project Leader: atmospheric chemical modelling.
- Nosal, M.; University of Calgary, Department of Mathematics and Statistics, Calgary, Alberta: Project Leader, data management.
- Peake, E.; University of Calgary, Kananaskis Centre for Environmental Research, Calgary, Alberta: Project Leader, atmospheric deposition and chemical analysis.
- Picard, R.J.; Western Research, Calgary, Alberta: Project Leader, emissions inventory.
- Rhodes, E.C.; University of Calgary, Department of Geography, Calgary, Alberta: geographical/meteorological information.
- Snider, C.; Western Research, Calgary, Alberta: Project Leader, air monitoring.
- Strosher, M.; University of Calgary, Kananaskis Centre for Environmental Research, Calgary, Alberta: Project Leader, sulphur gases and organics.
- Turchenek, L.W.; Alberta Research Council, Terrain Science Department, Edmonton, Alberta: soil chemistry modelling.
- Winchester, J.W.; Florida State University, Department of Oceanography, Tallahassee, Florida: elemental analysis data handling.

In addition, the research team included the authors of the literature reviews listed on pages 2 and 3.

It is intended that the research carried out to Critical Point I. serve as a model for continued studies on the environmental consequences of acidic and acidifying pollutants and air pollution in general.

**A.H. Legge,**
**Principal Investigator**

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## 1. INTRODUCTION

Alberta's industrial emissions and regulations are among the world's most stringent; however, there is public concern about the possible impact of emissions on air, land, water, and human systems (Alberta Government/Industry Acidic Deposition Research Program, Researching Acid Deposition: Workshop Proposals, Acid Deposition Research Program, June 1984). In a proactive step, the Alberta Government and industry jointly established the Acid Deposition Research Program (ADRP) in 1983 with the following goals:

a. To provide a comprehensive understanding of the effects and consequences of acid-forming gases on the environment;

b. To provide a scientific basis for sound, long-term environmental management and regulatory control with respect to acid-forming gases;

c. To disseminate such information to the Members Committee of the ADRP, to the public, and to government bodies;

d. To undertake any research deemed appropriate; and

e. To encourage and include opportunities for public representation in the ADRP.

Within the ADRP framework, the biophysics research effort was initiated in 1985 with the work planned for two phases which were designated by their terminal points, Critical Point I. and Critical Point II. Results and conclusions to Critical Point I. would in turn shape the second phase of the investigation.

The objectives of Critical Point I. are to answer the questions:

a. Are there at present observed or measurable adverse effects of acidic or acidifying pollutants on Alberta's vegetation, soils, and surface waters?

b. If the answer to (a.) is negative, when, where, and under what circumstances could such adverse effects occur in Alberta?

In addressing these two questions, the ADRP Biophysics Research Program was designed to characterize Alberta air quality (background and polluted) and to apply the resulting data in the assessment and prediction of regional-scale effects of various air pollutant exposure scenarios on sensitive environmental components. It is critical to note that the ADRP was not designed to address the effects of specific point sources but rather to develop a regional-scale assessment of environmental effects within the Province of Alberta.

The research to Critical Point I. was planned as a three and one-half year study (February 1985 - July 1988). The following steps were involved in this effort:

a. Critical review of world literature on cause-and-effect relationships of acidic and acidifying air pollutants with reference to crops, forests, soils, surface waters, and their related components;

b. Comprehensive characterization of background air quality (incoming air) of Alberta;

c. Comprehensive characterization of an environment within Alberta influenced by area, line, and local point sources of pollutants;

d. Preparation of a detailed, provincial-scale emission inventory of the oxides of sulphur and nitrogen; and

e. Development of regional-scale air quality predictions and application of such data toward regional-scale environmental effects assessment (crops, soils, and surface waters). In the effects assessment, forest response evaluations were excluded; a literature review on this subject was completed but no further work was mandated by the ADRP terms of agreement, since other agencies in Alberta were studying the subject and necessary data bases were not available during the course of this program.

Over 30 professional scientists and their support personnel participated in the study, representing a variety of disciplines such as atmospheric and analytical chemistry, meteorology, statistics and computer applications, crop and tree biology, soil and aquatic chemistry, and ecological modelling.

## Critical Review of World Literature on the Effects of Acidic and Acidifying Air Pollutants on Selected Environmental Components

The following peer reviewed literature reviews (10 volumes) and an overview document of the literature reviews (Volume 11) were released to the public during 1987:

•ADRP-B-01-87 Telang, S.A. 1987.
**Surface Water Acidification Literature Review.** Prep. for the Acid Deposition Research Program by the Kananaskis Centre for Environmental Research, The University of Calgary, Calgary, Alberta, 123 pp.
ISBN 0-921625-03-0 (Volume 1)

•ADRP-B-02-87 Visser, S., R.M. Danielson, and J.F. Parr. 1987.
**Effects of Acid-Forming Emissions on Soil Microorganisms and Microbially-Mediated Processes.** Prep. for the Acid Deposition Research Program by the Kananaskis Centre for Environmental Research, The University of Calgary, Calgary, Alberta, and U.S. Department of Agriculture, Beltsville, Maryland, 86 pp.
ISBN 0-921625-04-9 (Volume 2)

•ADRP-B-03-87 Krouse, H.R. 1987.
**Environmental Sulphur Isotope Studies in Alberta: A Review.** Prep. for the Acid Deposition Research Program by the Department of Physics, The University of Calgary, Calgary, Alberta, 89 pp.
ISBN 0-921625-05-7 (Volume 3)

•ADRP-B-04-87 Laishley, E.J. and R. Bryant. 1987.
**Critical Review of Inorganic Sulphur Microbiology with Particular Reference to Alberta Soils.** Prep. for the Acid Deposition Research Program by the Department of Biology, The University of Calgary, Calgary, Alberta, 50 pp.
ISBN 0-921625-06-5 (Volume 4)

•ADRP-B-05-87 Turchenek, L.W., S.A. Abboud, C.J. Tomas, R.J. Fessenden, and N. Holowaychuk. 1987.
**Effects of Acid Deposition on Soils in Alberta.** Prep. for the Acid Deposition Research Program by the Terrain Sciences Department, Alberta Research Council, Edmonton, Alberta, 202 pp.
ISBN 0-921625-07-3 (Volume 5)

•ADRP-B-06-87 Jaques, D.R. 1987.
**Major Biophysical Components of Alberta.** Prep. for the Acid Deposition Research Program by Ecosat Geobotanical Surveys Inc. North Vancouver, British Columbia, 108 pp. + maps
ISBN 0-921625-03-1 (Volume 6)

•ADRP-B-07-87 Campbell, K.W. 1987.
**Pollutant Exposure and Response Relationships: A Literature Review, Geological and Hydrogeological Aspects.** Prep. for the Acid Deposition Research Program by Subsurface Technologies and Instrumentation Limited, Calgary, Alberta, 151 pp. + maps.
ISBN 0-921625-09-X (Volume 7)

•ADRP-B-08-87 Torn, M.S., J.E. Degrange, and J.H. Shinn. 1987.
**The Effects of Acidic Deposition on Alberta Agriculture: A Review.** Prep. for the Acid Deposition Research Program by the Environmental Sciences Division, Lawrence Livermore National Laboratory, Livermore, California, 160 pp.
ISBN 0-921625-10-3 (Volume 8)

•ADRP-B-09-87 Mayo, J.M. 1987.
**The Effects of Acid Deposition on Forests.** Prep. for the Acid Deposition Research Program by the Department of Biology, Emporia State University, Emporia, Kansas, 74 pp.
ISBN 0-921625-11-1 (Volume 9)

•ADRP-B-10-87 Krupa, S.V. and R.N. Kickert. 1987.
**An Analysis of Numerical Models of Air Pollutant Exposure and Vegetation Response.** Prep. for the Acid Deposition Research Program by the Department of Plant Pathology, University of Minnesota, St. Paul, Minnesota, and Consultant, Corvallis, Oregon, 113 pp.
ISBN 0-921625-12-X (Volume 10)

•ADRP-B-11-87 Legge, A.H. and R.A. Crowther. 1987.
**Acidic Deposition and the Environment: A Literature Overview.** Prep. for the Acid Deposition Research Program by the Kananaskis Centre for Environmental Research, The University of Calgary, and Aquatic Resource Management, Calgary, Alberta, 235 pp.
ISBN 0-921625-13-8 (Volume 11)

## 2. COMPREHENSIVE CHARACTERIZATION OF THE BACKGROUND AIR QUALITY OF ALBERTA

> "To relate observed air quality conditions to emissions, and to forecast future pollutant concentrations, **it is necessary to monitor the composition of the air entering the Province of Alberta from the outside, as well as the chemistry of precipitation from clouds formed in this air.** This 'background air quality' is by no means constant; air from parts of the United States will have a different composition than air from British Columbia, and both will differ from air from the Northwest Territories. In addition, individual sources will give rise to variations in composition of air from each of these three major areas. Accordingly, a fixed station is needed, located near the British Columbia border, representing the most frequent source area of influent air." (Alberta Government/Industry Acid Deposition Research Program, Researching Acid Deposition: Workshop Proposals, Acid Deposition Research Program, June 1984).

Thus, **a background air quality monitoring station was established at Fortress Mountain**, Alberta (50°49′40″ - 115°12′20″). Dry and wet air pollutants (in the latter case, rain only) and meteorological parameters were measured at this site **for two full years** during 1985-1987.

**Fortress Mountain** is located in southwest Alberta (Figure 1), a region with $NO_x$ and $SO_2$ emissions of 2.6 and 4.2 tonnes $day^{-1}$, respectively, which constitute only 0.3% of the total provincial emissions. The monitoring site was within subalpine and alpine ecoregions at an elevation of 2103 m MSL, within mountainous terrain. Elevations of the valley floor, ridge, and mountain peaks of the surrounding area were approximately 1200, 2100, and 3000 m, respectively. Figures 2 and 3A show the site from two perspectives; Figure 3B shows the interior of the air quality monitoring station.

**Most of the time the air at the Fortress Mountain site was sufficiently pure that, for the majority of gases measured** (eg. $SO_2$, NO, $NO_2$, $H_2S$), **the automated monitors recorded concentration values below their reliable limits of detection.** To a somewhat lesser degree this was also true of the other two monitoring sites which are discussed below. This raised a serious problem: How does one characterize the average, median, or any other aggregate property of a set of measurements, when, for example, only the largest 5% of the values have been reliably measured?

Careful examination showed that the available data best fit a family of statistical frequency distributions called the Weibull distribution. Other researchers have increasingly recommended this approach even though it is more difficult mathematically than the more commonly used lognormal distribution. **A Weibull distribution was fit to the available data.** The fitted distribution was then used to deduce the balance of the values that were too small to

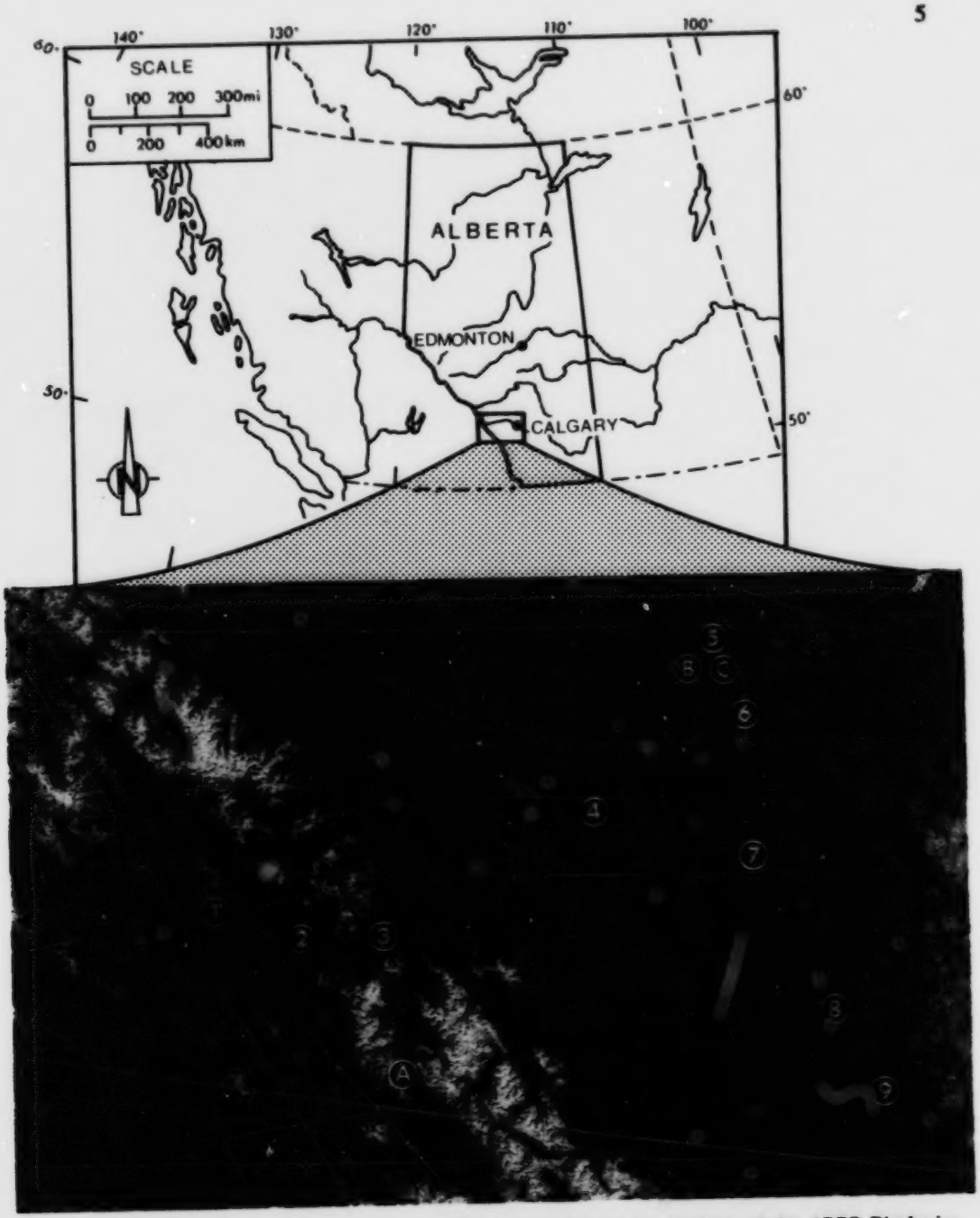



**Figure 1.** Map of western Canada and colour satellite image showing the locations of the ADRP Biophysics Research air quality and meteorological monitoring stations (A, B, C) along with major towns and cities (1 to 9). The air quality and meteorological monitoring stations are identified as (A) **Fortress Mountain**, (B) **Crossfield West**, and (C) **Crossfield East**. The towns and cities are identified as (1) Banff, (2) Canmore, (3) Exshaw, (4) Cochrane, (5) Crossfield, (6) Airdrie, (7) Calgary, (8) Okotoks, and (9) High River. The Rocky Mountains are seen to the left, while the agricultural land is seen to the right as the patch-work pattern. The satellite image is a combination of images acquired on September 28, 1985, and on September 6, 1986 by LANDSAT 5. The scale of the image is approximately 1:1,200,000. Satellite image of Calgary courtesy of Advanced Satellite Productions Inc. and Canada Centre for Remote Sensing Company.

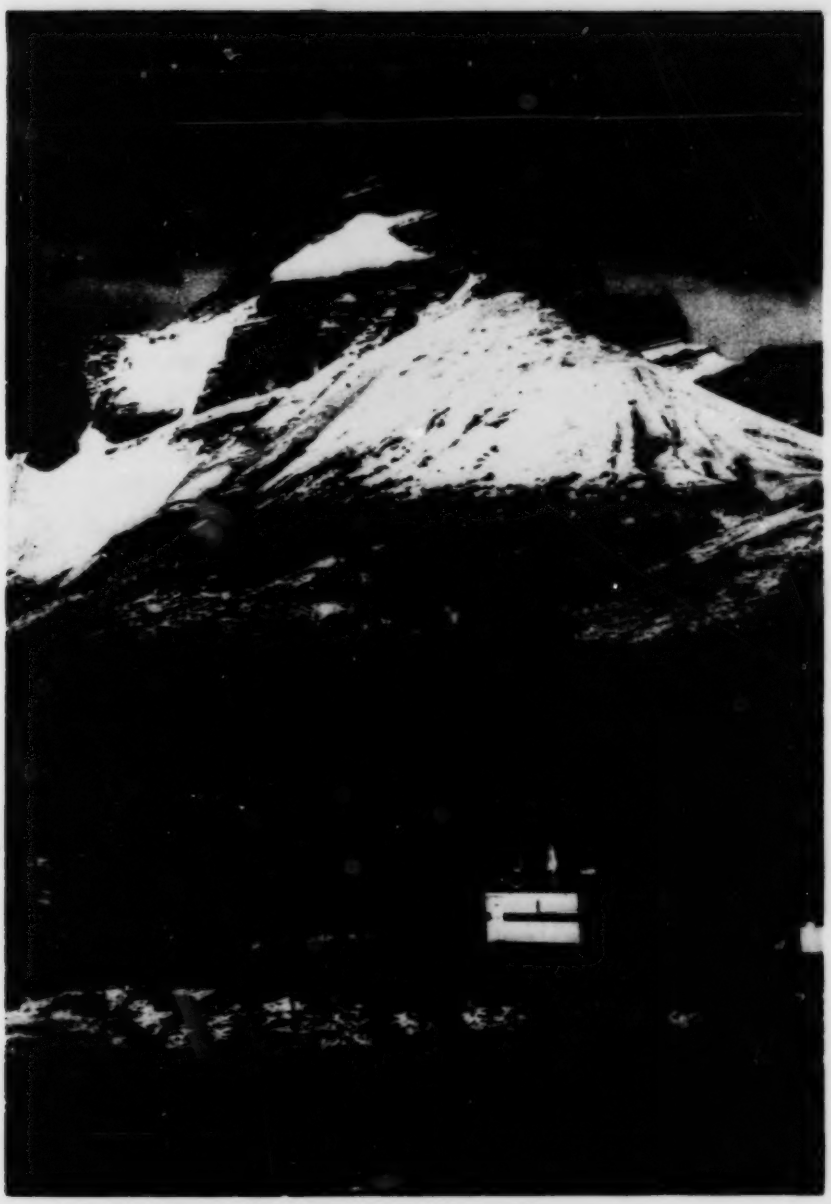


**Figure 2.** View from a helicopter, looking west of the **Fortress Mountain**, Alberta, air quality monitoring station.

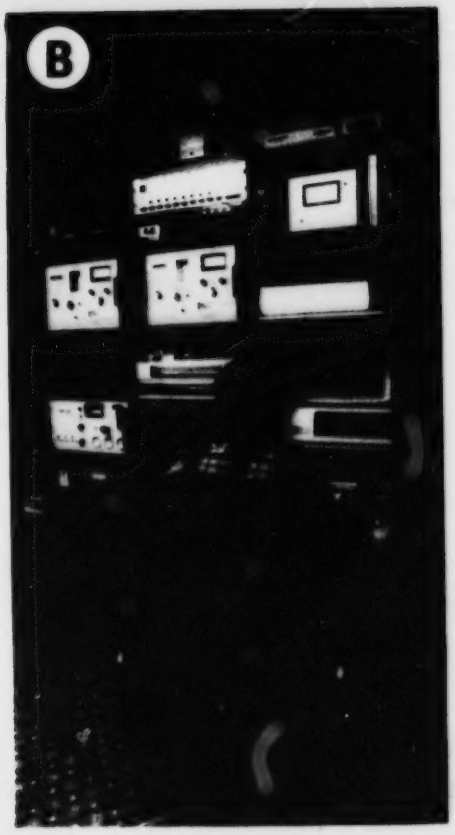



**Figure 3.** (A) View from a helicopter, looking north, of the **Fortress Mountain** air quality monitoring station. (B) Wide angle view inside the air quality monitoring station showing the station computer operator and the rack-mounted air quality and meteorological instrumentation.

measure. Obviously this approach could not be used, for example, to predict the concentration of $SO_2$ at 1000 hours on February 16, 1987; however, it could reveal that, with very high probability, a certain hourly average concentration occurred at least 30 times during the 2-year period. This later application is important; it lends confidence to the statements that follow.

Table 1 shows the statistical properties of the data from all automated instruments, aggregated as 1-hour averages for the entire 2-year period at **Fortress Mountain**. The 10-minute mean and hourly mean concentrations were identical to each other during each year for $SO_2$, $H_2S$, NO, $NO_2$, and $O_3$. Similarly, the median 10-minute or 1-hour pollutant concentrations during the first year were identical to the corresponding values for the second year. **These results suggest that the overall air quality at Fortress Mountain was homogeneous when only smoothed annual characteristics were considered**. Table 2 provides a comparison of the mean hourly pollutant concentrations observed over the two years (1985-1987) at **Fortress Mountain** with the corresponding values reported in the literature for unpolluted or least polluted sites (remote or rural). **The mean hourly concentrations at Fortress Mountain for $SO_2$, $NO_2$, and $O_3$ were below or nearly equal to the concentrations reported for other remote sites**. The concentrations of other pollutants were within the range reported for rural sites. These relatively high values for $H_2S$ and NO were most likely due to mathematical bias caused by the great number of observations with values below the detection limit. **Nevertheless, Fortress may be considered representative of an acceptable background air quality site for Alberta and possibly for northwestern North America**.

As opposed to the smoothed (annual mean) pollutant statistics, the range and percentiles of pollutant concentrations, both 10-minute and 1-hour, varied between the two monitoring years. This is to be expected due to the stochasticity and variability in the climatic data at any given site between years. The computations of long-term means tend to mask the underlying pollutant episodicity.

At the **Fortress Mountain site** while the mean **hourly $O_3$** concentrations were **40.9 ppb and 45.8 ppb**, respectively, during **1985-1986** and **1986-1987**, corresponding maximum concentrations were **70.9** and **122.4 ppb**.

**The high $O_3$ maxima of 1987 were associated with episodes occurring on two or more consecutive days, each time during the period between April 15 and June 30, 1987**. Such $O_3$ episodes were observed for approximately 14 days of the 45-day period examined (Table 3).

Cumulative daily average, 1-hour pollutant concentrations, and surface meteorological parameters were evaluated for the 14 $O_3$ episode versus 14 non-episode days at **Fortress Mountain**. With the exception of the $O_3$ concentrations, values for all other parameters,

**TABLE 1.** Summary statistics of automated gaseous pollutant measurements and meteorological variables.* Sampling location: Fortress Mountain. Sampling period: 1985-87. Time resolution of data: 1 hour.

| Variable | (n) | Mean | S.D. | Range | | Median | Percentile | | | | | | Skewness | Kurtosis |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Min. | Max. | | 10 | 30 | 70 | 90 | 95 | 99 | | |
| 1. $SO_2$ | 15207 | .16 | .61 | .00 | 14.8 | .10 | .00 | .10 | .10 | .20 | .20 | .90 | 13.5 | 207.1 |
| 2. $H_2S$ | 15227 | .55 | .11 | .10 | 5.7 | .50 | .40 | .50 | .60 | .70 | .70 | .80 | 12.2 | 499.3 |
| 3. NO | 16494 | .52 | .21 | .00 | 7.2 | .50 | .40 | .40 | .60 | .70 | .70 | 1.1 | 10.4 | 211.7 |
| 4. $NO_2$ | 15816 | 1.2 | .43 | .10 | 13.0 | 1.1 | .90 | 1.1 | 1.2 | 1.4 | 1.5 | 3.0 | 9.2 | 129.6 |
| 5. $CO_2$ | 16891 | 345.4 | 8.0 | 312.2 | 381.3 | 346.9 | 335.1 | 341.1 | 350.0 | 354.0 | 355.8 | 364.0 | - .37 | 1.1 |
| 6. $O_3$ | 16850 | 43.4 | 12.4 | 2.8 | 122.4 | 41.2 | 30.3 | 37.1 | 46.7 | 59.4 | 67.4 | 84.2 | 1.2 | 2.8 |
| 7. Wind Speed | 16971 | 14.5 | 8.9 | .00 | 78.4 | 13.5 | 4.1 | 9.4 | 18.0 | 25.7 | 30.2 | 43.5 | 1.1 | 2.4 |
| 8. Wind Direction | 16995 | 200.6 | 55.5 | 1.00 | 352.7 | 199.9 | 156.0 | 180.9 | 225.7 | 261.0 | 285.5 | 328.6 | - .84 | 2.3 |
| 9. Temperature | 16993 | 2.2 | 8.9 | -33.00 | 24.4 | 1.9 | - 8.00 | - 2.30 | 7.4 | 13.7 | 15.9 | 19.3 | - .46 | .55 |
| 10. Barometric Pressure | 16994 | 783.2 | 7.3 | 748.0 | 813.8 | 784.0 | 773.3 | 780.0 | 787.5 | 792.0 | 794.0 | 797.0 | - .62 | .76 |
| 11. Precipitation | 12103 | .00 | .01 | .00 | .40 | .00 | .00 | .00 | .00 | .00 | .00 | .00 | 17.6 | 428.8 |
| 12. Humidity | 16538 | 36.0 | 8.9 | 20.0 | 78.8 | 35.2 | 24.7 | 31.0 | 40.4 | 47.8 | 51.5 | 58.2 | .53 | .46 |
| 13. Radiation | 15454 | 319.1 | 468.2 | - 2.00 | 2154.3 | 37.8 | .00 | .00 | 384.8 | 1077.2 | 1380.6 | 1789.3 | 1.5 | 1.4 |

* All gas concentrations in ppb, except $CO_2$ (ppm); wind speed: km $h^{-1}$; wind direction: degrees; temperature: °C; pressure: mbars; precipitation: mm; humidity: %; radiation: Langleys $min^{-1}$.

**TABLE 2.** A comparison of mean hourly pollutant concentrations at **Fortress Mountain** (1985-1987) with values published in the literature for remote and rural locations. All concentrations in **ppb.**

| Pollutant | Remote Locations* | Fortress Mountain | Rural Locations* |
|---|---|---|---|
| $SO_2$ | <1.0 | 0.16 | 1.0 - 30 |
| $H_2S$ | 0.05 - 0.10 | 0.55 | - |
| NO | <0.05 | 0.52 | 0.05 - 20 |
| $NO_2$ | <1.0 | 1.2 | 1.0 - 20 |
| $O_3$ | <50 | 43 | 20 - 80 |

* Values reported in a number of published papers by other scientists.

**TABLE 3.** Characteristics of representative $O_3$ episode versus non-episode days at **Fortress Mountain, 1987.**

| Episode | | | Non-Episode | | |
|---|---|---|---|---|---|
| Date | Highest $\bar{x}$ Hourly $O_3$ (ppb) | Time | Date | Highest $\bar{x}$ Hourly $O_3$ (ppb) | Time |
| Apr 24 | 93.5 | 1800 | Apr 23 | 66.5 | 0300 |
| Apr 25 | 89.3 | 0100 | Apr 28 | 68.1 | 1300 |
| Apr 26 | 86.8 | 1200 | Apr 29 | 63.5 | 2400 |
| May 12 | 105.8 | 2400 | May 05 | 81.1 | 2400 |
| May 13 | 122.4 | 0100 | May 10 | 72.6 | 0100 |
| May 25 | 113.4 | 2200 | May 21 | 63.2 | 0400 |
| May 26 | 101.1 | 0100 | Jun 04 | 67.6 | 1500 |
| May 27 | 108.3 | 1200 | Jun 08 | 69.7 | 0200 |
| May 28 | 107.6 | 2000 | Jun 09 | 49.2 | 2400 |
| May 29 | 107.3 | 1000 | Jun 11 | 56.4 | 2400 |
| May 30 | 110.3 | 0400 | Jun 13 | 66.0 | 1700 |
| May 31 | 100.3 | 1100 | Jun 16 | 68.8 | 1400 |
| Jun 06 | 102.7 | 0800 | Jun 22 | 52.8 | 0100 |
| Jun 07 | 91.4 | 0100 | Jun 30 | 53.3 | 0700 |

including humidity, were very comparable in the two categories. **These results suggested that the observed high $O_3$ concentrations most likely were not due to local, photochemically generated $O_3$ or to subsidence from the stratosphere.** The correlation coefficients (r) between $NO_2$:NO versus $O_3$ were <0.02, independent of the range of $O_3$ concentration (<50.0 ppb; 50.1-90.0 ppb or >90.1 ppb) used in the statistical analysis.

Air trajectory analyses elucidated the geographic origin of air masses corresponding to $O_3$-episode and non-episode periods at **Fortress Mountain. With one exception, an easterly flow from the Calgary area, $O_3$ episodes at Fortress Mountain were governed by air**

masses originating from the west and southwest (British Columbia and the State of Washington). In contrast, on non-episode days wind speeds were low and flow directions were less well defined. The consistency of these trajectories, the high humidity in the context of stratospheric air mass, and the consistent diurnal pattern on episode days, as discussed below, makes it unlikely that the high ozone concentrations originated in the stratosphere.

Both on episode and non-episode days at the Fortress Mountain site the diurnal $O_3$ profiles (Figure 4) were not typical of the known patterns from the literature. During the daytime, high $O_3$ concentrations occurred between roughly 1100 and 1500 hours and then decreased during subsequent hours. On days of $O_3$ episode, concentrations then increased again sharply into the nighttime. A similar pattern was observed on non-episode days, but with a longer period of decrease, a later maximum, and lower $O_3$ concentrations.

The periods of rise in $O_3$ concentrations during the day (0800-1000 to 1300-1400 hours), the subsequent decrease, and the occurrence of much higher concentrations mostly at night appeared to be consistent with the patterns of diurnal changes in synoptic versus katabatic air flows in the mountains and the adjacent Kananaskis Valley. It is concluded that these ozone episodes are the result of long-range $O_3$ transport, rather than either local generation of ozone or stratospheric intrusion.

Because of the nature of the computation, these diurnal patterns were not observed when $O_3$ concentration was averaged for each hour of the day cumulatively for each year or for the two study years. The flat diurnal profile observed in this type of computation was similar to that previously reported for other high elevation sites such as the Whiteface Mountain, New York, and Whitetop Mountain, Virginia.

In addition to the near-continuous measurements of the major pollutants ($O_3$, $NO_2$, NO, $SO_2$, and $CO_2$), reduced sulphur species (COS, $CS_2$, and $H_2S$) and also $SO_2$ were measured through conventional and cryogenic sampling and gas chromatography (Table 4).

**TABLE 4.** Comparison of the ambient concentrations of sulphur gases at Fortress Mountain with values reported in the literature for global background concentrations.

| | Concentration range (ppb) | |
|---|---|---|
| Sulphur Species | Fortress Mountain | Global Background* |
| COS | 0.23 - 0.42 | 0.10 - 0.56 |
| $CS_2$ | 0.012 - 0.026 | 0.07 - 0.37 |
| $H_2S$ | 0.044 - 0.099 | 0 - 0.32 |
| $SO_2$ | 0.25 - 0.96 | 0.05 - 0.34 |

* Adapted from Sze, N.D. and K.W. Ko, *Atmospheric Environment* 14: 1223-1239 (1980).

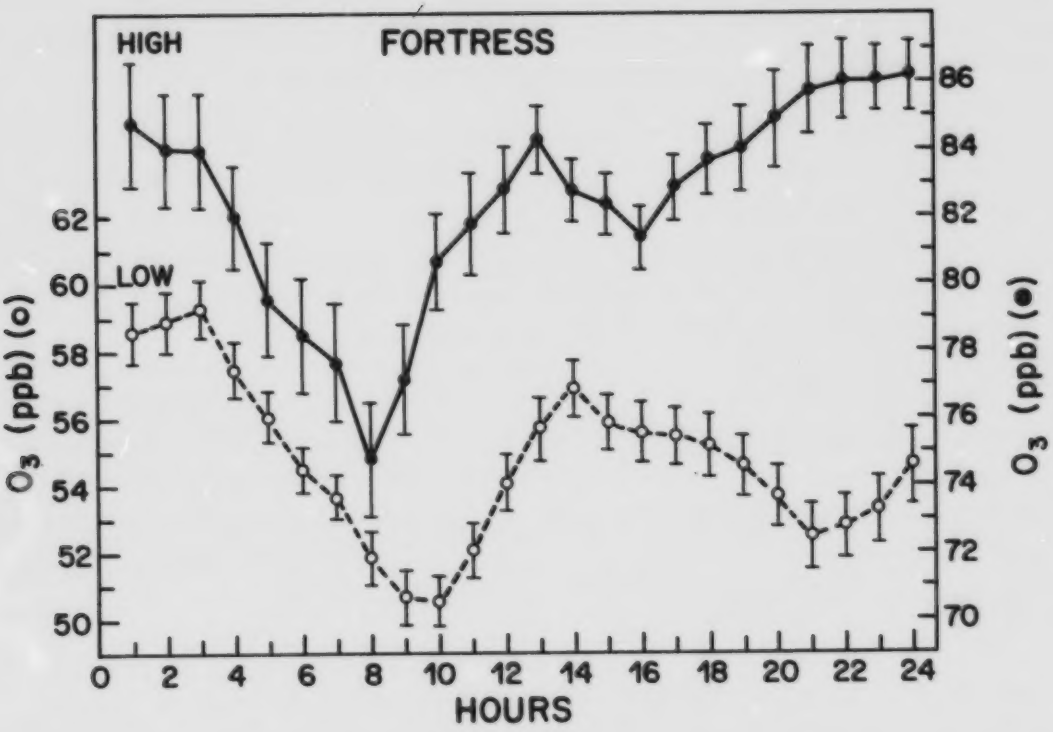



**Figure 4.** Diurnal $O_3$ profiles on episode (high) and non-episode (low) days at Fortress Mountain. The vertical bars represent S.D. of the mean for each hour.

A serial annular denuder-filter pack system (Kananaskis Atmospheric Pollutant Sampler, KAPS) was also used to measure integrated 48-hour ambient concentrations of $SO_2$, $HNO_2$, $HNO_3$, $NH_3$ and fine (<2.5 μm) particulate $NO_3^-$ and $SO_4^{2-}$ at Fortress Mountain (Table 5).

**TABLE 5.** Air concentrations of chemical species that contribute to acidic dry deposition: A comparison of values obtained at Fortress Mountain with the corresponding values in the published literature.

| | Range of concentrations (μg $m^{-3}$) | |
|---|---|---|
| Chemical Species | Fortress Mountain | Typical Ambient Concentrations* |
| $SO_2$ | 0.0003 - 16.9 | 0.20 - 30 |
| $HNO_2$ | 0.0005 - 0.46 | 0.20 - 2.0 |
| $HNO_3$ | 0.0005 - 3.4 | 0.10 - 15 |
| $NH_3$ | 0.04 - 1.3 | 0.10 - 20 |
| $NO_3^-$ | 0.02 - 0.66 | 0.10 - 10 |
| $SO_4^{2-}$ | 0.05 - 2.0 | 0.20 - 40 |

* Reported by Stevens, R.K., in: EPA Report 600/9-86/014 (1986)

**The results presented in Tables 4 and 5 further show that the air quality at Fortress Mountain, with the exception of the $O_3$ episodes, can be considered to be representative of the true regional background.** However, as shown in the case of $O_3$, an area being classified as remote does not rule out the possibility of occasional long-range transport of air pollutants to that site.

Elements of anthropogenic origin such as S, As, and Pb were in higher concentrations in the fine (<2.5 μm) compared to the coarse (>2.5 μm) particle fraction at Fortress Mountain. Table 6 provides a comparison of the S, Pb, and Br concentrations at Fortress Mountain with values reported for the Canadian Arctic and a polluted site in southern Sweden.

**TABLE 6.** Comparison of the annual means of S, Pb, and Br concentrations at Fortress Mountain with values from the Canadian Arctic and southern Sweden.

| | Mean Concentration ng $m^{-3}$ | | |
|---|---|---|---|
| Sampling Location | S | Pb | Br |
| Fortress Mountain* | 297 | 2.8 | 1.4 |
| Canadian Arctic** | 297 | 2.7 | 7.9 |
| S. Sweden | 800 | 21 | — |

* Fine and coarse particles combined, as the other two studies did not report actual particle sizes.

** Average of three sampling sites. Data for the Arctic and Sweden extracted from Barrie, L.A. and R.M. Hoff. *Atmospheric Environment* 19: 1995-2010 (1985).

The values of S concentrations smoothed as annual means and their similarity between **Fortress Mountain** and the three combined Canadian Arctic sites suggest homogeneity in regional-scale air quality of the Canadian background sites. This observation was also similar for the Pb concentrations. However, mean Br concentrations were vastly different between **Fortress Mountain** (low) and the Canadian Arctic sites (high). In general, Br is considered to be an indicator of emissions from mobile sources. However, given the geographic locations of the Canadian Arctic sites, Barrie and Hoff (Table 6) concluded that the Br at those sites was contributed by both sea salt and anthropogenic sources.

**The mean pH of rain at Fortress Mountain (pH 4.73) was comparable to values (pH 4.78 - 4.96) reported for five remote sites** by Galloway et al. (Journal of Geophysical Research 87: 8771-8786, 1982). At **Fortress Mountain** the correlation coefficients (r) between $H^+$ and $SO_4^{2-}$ and between $H^+$ and $NO_3^-$ were very low (0.13 and 0.18, respectively).

Much stronger correlations were obtained between $SO_4^{2-}$ and $K^+$, $Mg^{2+}$, $Ca^{2+}$ and $NH_4^+$ (r between 0.58 and 0.73) and $NO_3^-$ and $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ (r between 0.50 and 0.68). These results were further confirmed by principal component analysis where $SO_4^{2-}$, $NO_3^-$, and $Cl^-$ were grouped strongly with $Ca^{2+}$, $Mg^{2+}$, and $NH_4^+$ in a common factor (Factor 1) while $H^+$ was loaded high and negative in Factor 2 together with $Na^+$ and $Ca^{2+}$. These results suggested that **at Fortress Mountain most of the $SO_4^{2-}$ and $NO_3^-$ was not associated with acidity**. Independent of these characteristics, $SO_4^{2-}$ and $NO_3^-$ in rain were reasonably well correlated with each other (r 0.66). Even though average air concentrations of $SO_2$, NO, and $NO_2$ were in the ppb range at **Fortress Mountain**, ambient $HNO_3$ and $SO_2$ concentrations also showed reasonable correlation with the corresponding concentrations of $NO_3^-$ and $SO_4^{2-}$ in rain (r 0.56 and 0.66, respectively). However, based on the previous discussion, the contribution of these processes to rain acidity was considered to be minimal.

Measurements at **Fortress Mountain** clearly met the immediate objective of characterizing the quality of air entering Alberta, and of providing input for modelling of pollutant concentrations there. These measurements revealed **sporadic intrusion of high $O_3$ concentrations**, most likely by long-range transport from the west coastal cities in Washington and British Columbia. Otherwise, more than 95% of the time, **this is an excellent site for the measurement of the global background level of pollutants**, and it is unfortunate that the satisfaction of the short-range needs of ADRP has resulted in the interruption of this valuable time series of measurements. Finally, these data, together with those from the lower-altitude sites, have provided input for valuable studies of the statistical properties of air quality measurements.

## 3. COMPREHENSIVE CHARACTERIZATION OF AN ENVIRONMENT INFLUENCED BY EMISSIONS WITHIN ALBERTA

> "There is a need to consider questions of air quality at several different levels. Clearly, there is a need to relate Alberta industrial emissions to natural emissions and to the background air quality of the geographic region in which the province is located. Moreover, the environmental consequences of this modified air quality must be considered through effects of both primary and secondary pollutants (secondary pollutants are formed by chemical reactions in the air, involving actual emitted species, usually gaseous). Studies of air chemistry and its effects are not necessarily sufficient since precipitation quality will also be modified (by a largely unknown amount) by Albertan emissions; hence precipitation-related studies must also be considered." (Alberta Government/Industry Acidic Deposition Research Program, Researching Acid Deposition: Workshop Proposals, Acid Deposition Research Program, June 1984).

Thus, two air quality monitoring stations were established at **Crossfield, Alberta** (Figure 5). Both dry and wet air pollutants (in the latter case, rain only) and meteorological parameters were measured at the two sites for two full years during 1985-1987. These two monitoring sites, **Crossfield West** (51°23′1″ - 114°7′30″, 1158 m MSL) and **Crossfield East** (51°22′35″ - 114°1′0″, 1098 m MSL) were located in an urban airshed (40 km north of Calgary, Alberta) in the vicinity of a local sour gas processing plant (Figure 5). At least one of the two sites, **Crossfield East** was considered to be influenced by a major line source (Highway 2) and by a number of other local point sources. **Crossfield West** was considered to be the **upwind site** located approximately 6 km west-southwest of the gas plant, while **Crossfield East** was considered to be the **downwind site**, about 2.5 km southeast of the gas plant. Both sites were in the Fescue Grass ecoregion; total $NO_x$ and $SO_2$ emissions within this ecoregion were 152.7 tonnes $day^{-1}$ or 7.8% of the total provincial emissions. Figures 6-8 show different perspectives of the two Crossfield air quality monitoring sites.

As opposed to the background site at **Fortress Mountain** (20 - 30 ppb range), 10-minute maximum $SO_2$ concentrations at **Crossfield West** were in the 130 - 140 ppb range, while at **Crossfield East** they were in the 160 - 170 ppb range (Table 7). Further, the frequency of occurrences of $SO_2$ at **Crossfield East** was greater than at **Crossfield West**, reflecting its location close to a point source. Similar patterns were also observed with $H_2S$, NO, and $NO_2$.

The most striking feature of the $SO_2$ data at the two **Crossfield sites** is displayed in Figures 9 and 10, which are 3-dimensional plots of average hourly $SO_2$ concentration as a function of hour of the day and wind direction for each of the stations. For each case the impact of the local point source is obvious at the relevant wind direction, as is the tendency for

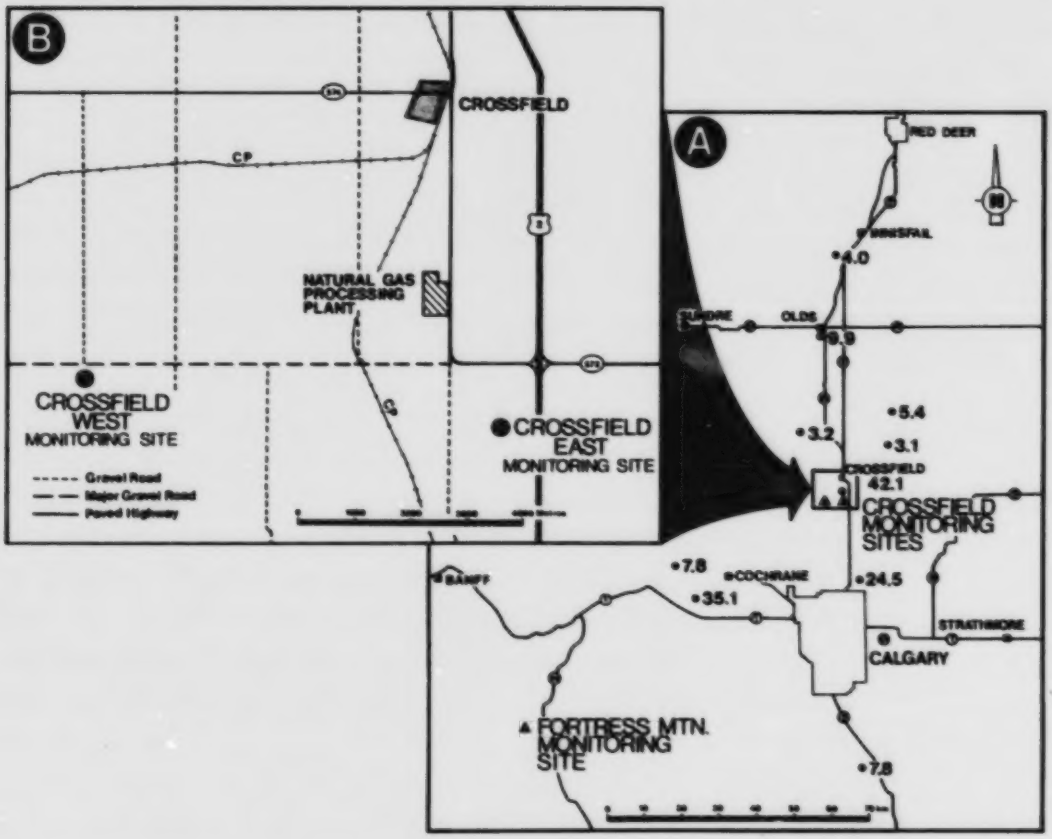
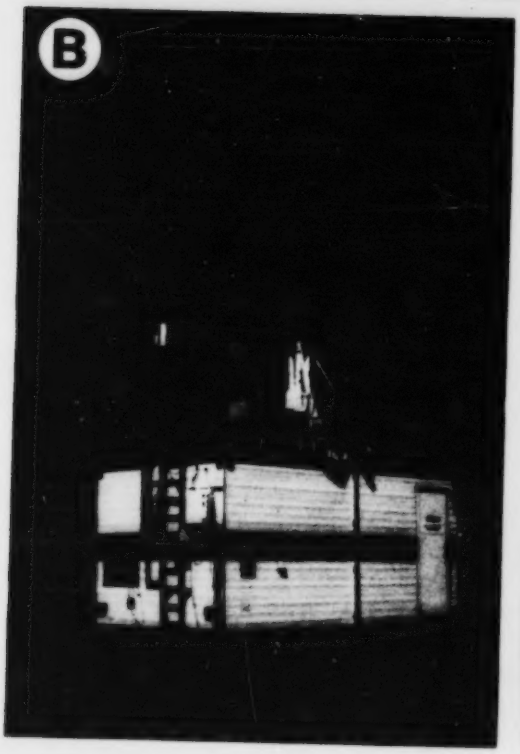



**Figure 5.** (A) Map showing the comparative geographic locations of the three ADRP air quality monitoring sites. Background air quality was monitored at Fortress Mountain. Sources of $SO_2$ (t $d^{-1}$) in the vicinity of the Crossfield monitoring sites are noted in the Figure. (B) A closer view of the geographic location of the two air quality monitoring sites in relation to Crossfield and the local point source of $SO_2$.

**Figure 6.** (opposite) (A) View from a helicopter, looking northeast, with the Crossfield West air quality monitoring station in the foreground and a gas plant in the background. (B) Closeup view of the Crossfield West air quality monitoring station. (C) View of rack-mounted air quality and meteorological instrumentation inside the Crossfield West air quality monitoring station.

A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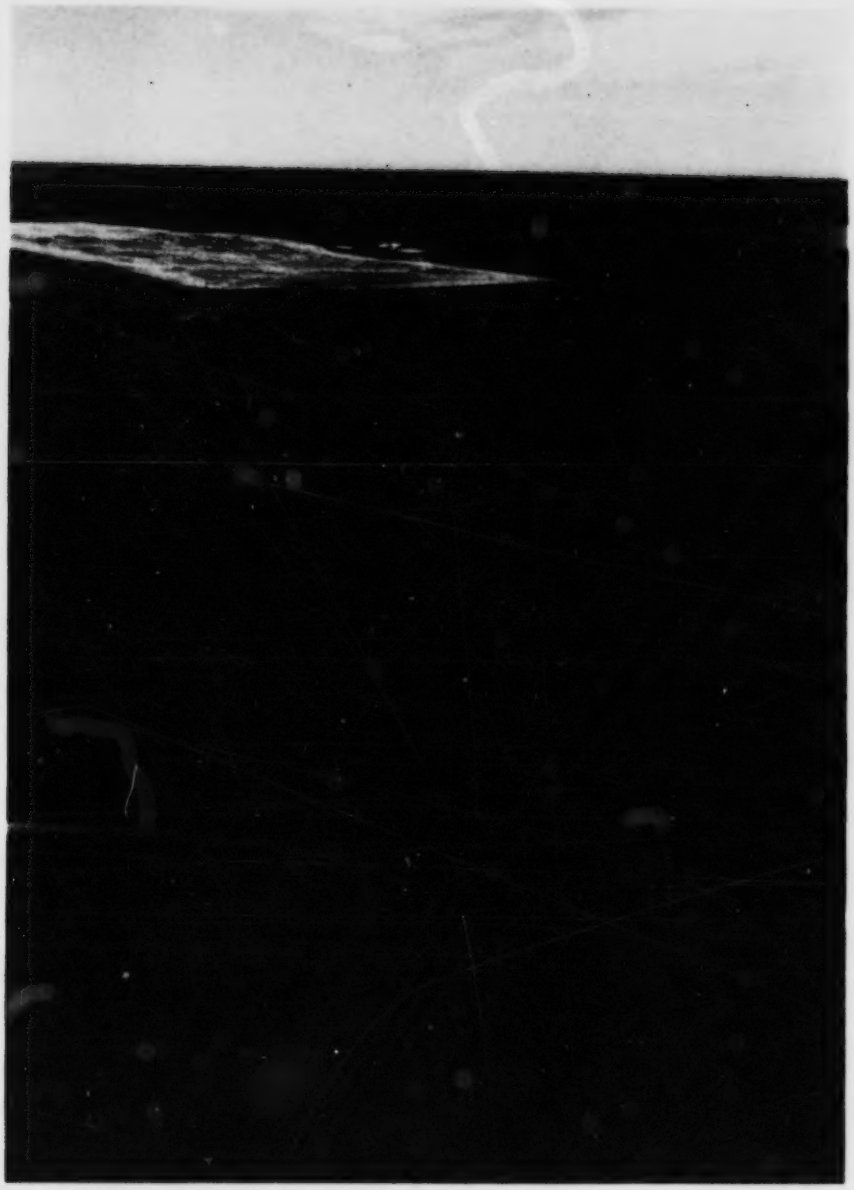

**Figure 7.** View from a helicopter, looking southeast, of the **Crossfield East** air quality monitoring station. Highway 2 is seen in the background.

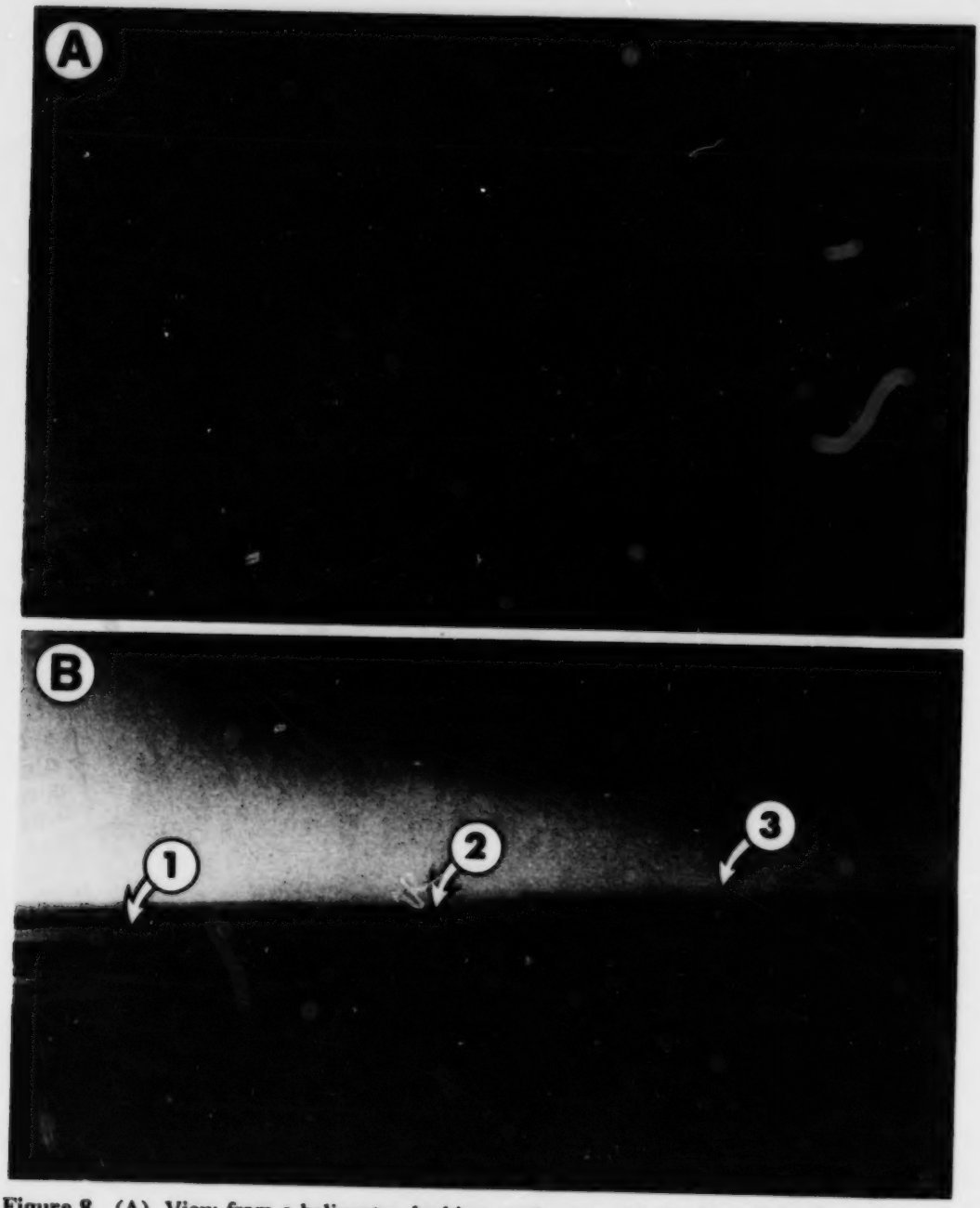


**Figure 8.** (A). View from a helicopter, looking northwest, with the **Crossfield East** air quality monitoring station. A gas plant is seen in the centre background with the Town of Crossfield to the right.

(B). View from a helicopter, looking south, with the Town of Crossfield in the foreground and a gas plant in the background. The location of Highway 2 is shown by (1) and the location of the **Crossfield East** air quality monitoring station is shown by (2). Urban haze over the City of Calgary is seen on the horizon (3).

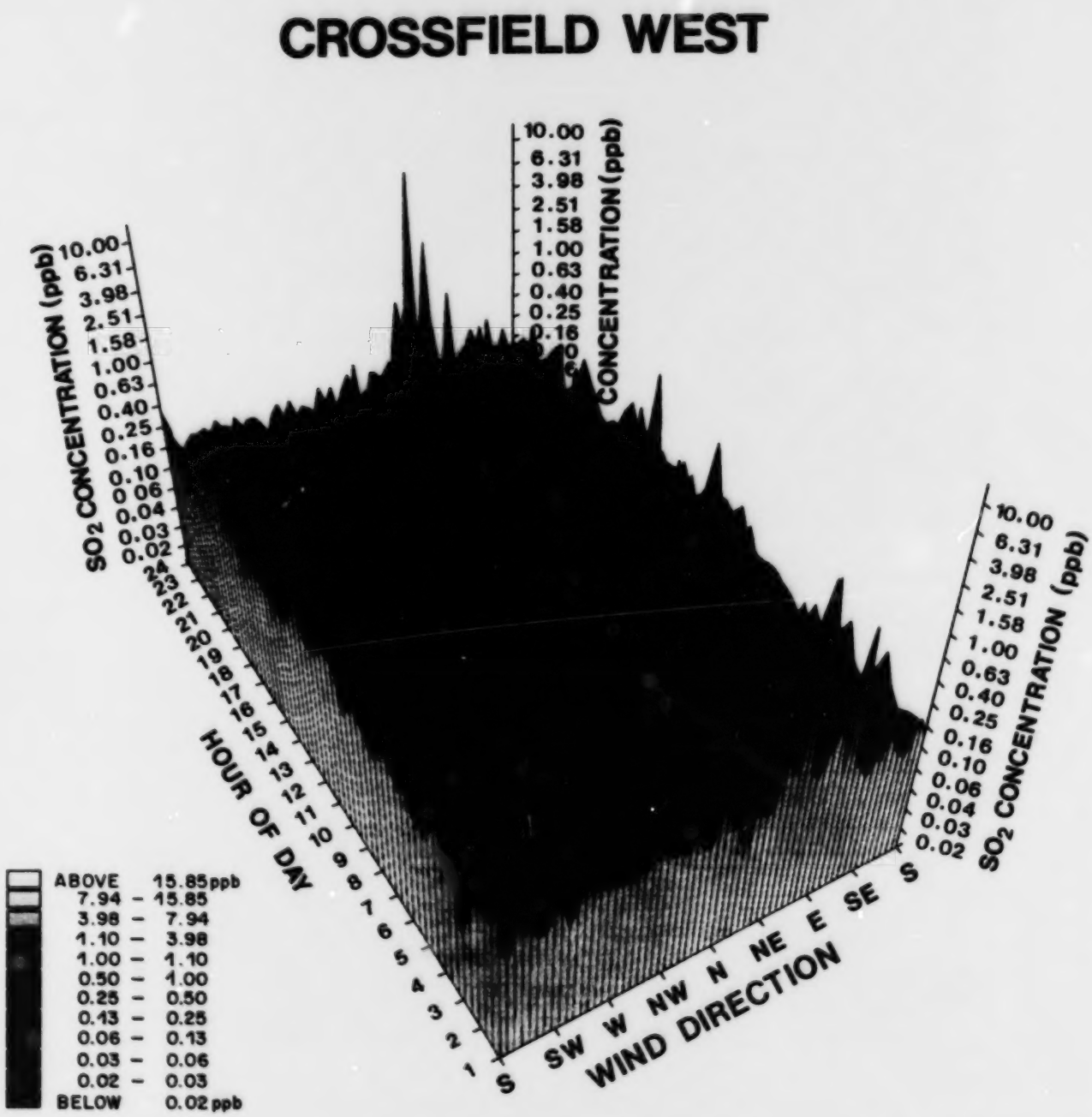


**Figure 9. Crossfield West:** Sulphur dioxide concentration as a function of the wind direction and hour of the day (November 1, 1985 - October 31, 1987).

# CROSSFIELD EAST

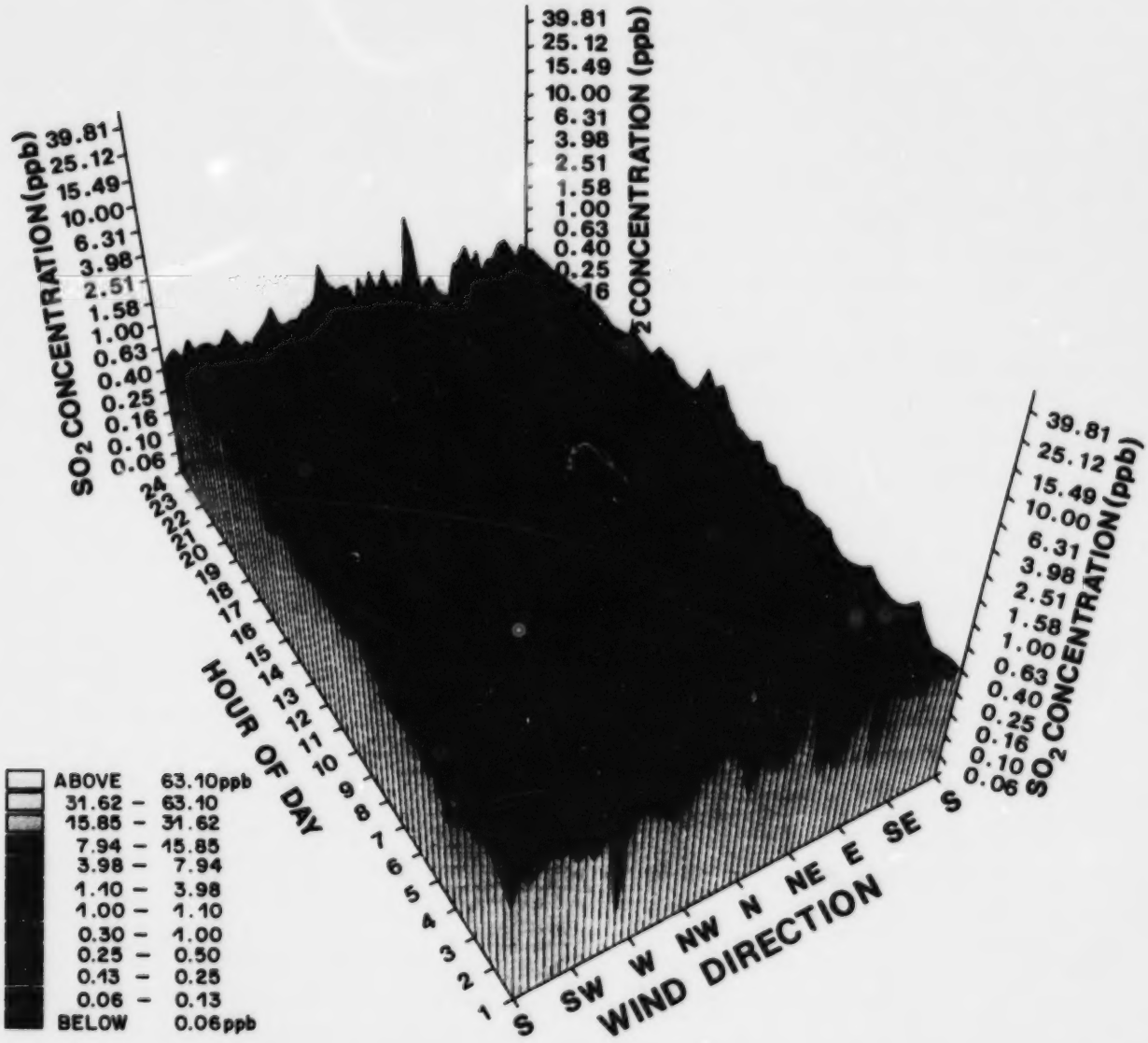


**Figure 10.** **Crossfield East:** Sulphur dioxide concentration as a function of the wind direction and hour of the day (November 1, 1985 - October 31, 1987).

**TABLE 7.** Comparison of pollutant concentrations at **Fortress Mountain** with the corresponding values at **Crossfield West** and **East** (1985-1987).

| Pollutant | Range of 10 Minute Concentrations (ppb) | | |
|---|---|---|---|
| | **Fortress Mountain** | **Crossfield West** | **Crossfield East** |
| $SO_2$ | 0** - 24 | 0 - 130 | 0 - 168 |
| $H_2S$ | 0 - 17 | 0 - 70 | 0 - 68 |
| NO | 0 - 23 | 0 - 103 | 0 - 280 |
| $NO_2$ | 0 - 17 | 0 - 59 | 0 - 81 |
| $O_3$ | 0 - 129 | 0 - 87 | 0.5 - 137 |
| $CO_2$* | 312 - 387 | 289 - 489 | 306 - 496 |

* Concentration in **ppm**

** Below the detection limit

the highest concentrations to occur late in the day. Calgary, as an area source, is sufficiently distant that it has no impact of consequence; presumably much of the $SO_2$ from the city has been either removed from the surface layer or converted into $SO_4^{2-}$. Tables 8 and 9 give the statistical properties of the continuous sampling data from **Crossfield West** and **Crossfield East**, respectively, expressed as hourly averages and compiled for the entire 2-year period.

The mean and median hourly concentrations of $O_3$ were at **Fortress Mountain** > **Crossfield West** > **Crossfield East**. At **Crossfield West**, while the mean hourly $O_3$ concentrations were, respectively, 23.9 ppb and 32.0 ppb during 1985-1986 and 1986-1987, corresponding **maximum** concentrations were **64.9 ppb** and **80.5 ppb**. These high hourly $O_3$ concentrations occurred during <1% of the total monitored time each year. In comparison, at **Crossfield East mean hourly $O_3$** concentrations ranged from **22.5 ppb** to **26.8 ppb** during the two years and the corresponding maximum concentrations were **66.1 ppb** and **73.8 ppb**, again occurring during <1% of the total monitored time each year. At the high elevation **Fortress Mountain** site, the **maximum hourly $O_3$** concentrations were **70.9 ppb** and **122.4 ppb**, respectively, during 1985-1986 and 1986-1987.

The $O_3$ episodes at **Fortress Mountain** occurred during April-June, 1987. High hourly $O_3$ concentrations also occurred at **Crossfield West** and **Crossfield East** during the same period. Table 10 provides values of highest hourly $O_3$ concentrations at **Crossfield West** and **East** on the same days identified as episode or non-episode days (Table 3) at **Fortress Mountain** (located at approximately 90 km southwest of the **Crossfield sites**). The differences in the highest hourly $O_3$ concentrations on episode versus non-episode days at the two **Crossfield sites** were not as dramatic (15-21%) as at **Fortress Mountain** (38%). Nevertheless, highest hourly $O_3$ concentrations on episode days were generally greater than non-episode day concentrations at the two **Crossfield sites**.

**TABLE 8.** Summary statistics of automated gaseous pollutant measurements and meteorological variables.* Sampling location: **Crossfield West.** Sampling period: 1985-1987. Time resolution of data: 1 hour.

| Variable | (n) | Mean | S.D. | Range | | Median | Percentile | | | | | | Skewness | Kurtosis |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Min. | Max. | | 10 | 30 | 70 | 90 | 95 | 99 | | |
| 1. $SO_2$ | 15859 | .56 | 2.4 | .00 | 84.3 | .20 | .10 | .10 | .20 | .40 | 1.8 | 9.6 | 14.7 | 322.1 |
| 2. $H_2S$ | 15089 | .28 | .66 | .00 | 34.4 | .20 | .10 | .20 | .30 | .40 | .40 | .60 | 33.2 | 1368.1 |
| 3. NO | 16424 | .38 | 2.2 | .00 | 89.5 | .10 | .00 | .10 | .20 | .30 | .40 | 8.1 | 16.7 | 432.1 |
| 4. $NO_2$ | 16416 | 2.8 | 4.2 | .10 | 51.3 | 1.2 | .80 | 1.00 | 1.8 | 6.7 | 10.2 | 22.9 | 4.2 | 23.2 |
| 5. $CO_2$ | 16442 | 347.4 | 11.2 | 291.1 | 462.2 | 346.9 | 333.9 | 342.0 | 352.2 | 361.0 | 366.2 | 377.7 | .57 | 2.9 |
| 6. $O_3$ | 16495 | 28.0 | 11.5 | 2.3 | 80.5 | 27.0 | 14.4 | 21.9 | 32.8 | 42.9 | 49.4 | 59.7 | .53 | .64 |
| 7. Wind Speed | 16632 | 14.6 | 9.1 | .00 | 72.4 | 13.2 | 4.2 | 9.2 | 18.0 | 26.6 | 31.6 | 41.8 | .98 | 1.6 |
| 8. Wind Direction | 16037 | 218.0 | 79.2 | 5.2 | 360.0 | 237.5 | 102.7 | 177.0 | 263.5 | 315.6 | 329.2 | 343.6 | - .58 | - .35 |
| 9. Temperature | 16466 | 4.9 | 10.2 | -34.80 | 33.2 | 5.8 | - 7.70 | .70 | 10.5 | 16.9 | 19.9 | 25.2 | - .65 | .87 |
| 10. Barometric Pressure | 16613 | 880.3 | 6.8 | 850.0 | 901.2 | 881.0 | 871.2 | 877.0 | 884.0 | 888.8 | 891.0 | 894.5 | - .34 | .19 |
| 11. Precipitation | 15095 | .001 | .01 | .00 | .30 | .00 | .00 | .00 | .00 | .00 | .00 | .00 | 15.3 | 289.0 |
| 12. Humidity | 15645 | 43.7 | 12.2 | 20.0 | 98.5 | 43.3 | 27.3 | 35.6 | 52.5 | 60.1 | 62.3 | 65.4 | - .006 | - 1.10 |
| 13. Radiation | 12387 | 354.3 | 493.5 | - 2.00 | 2058.1 | 65.4 | - 1.00 | .00 | 456.7 | 1202.1 | 1464.3 | 1761.0 | 1.4 | .71 |

* All gas concentrations in ppb, except $CO_2$ (ppm); wind speed: km $h^{-1}$; wind direction: degrees; temperature: °C; pressure: mbars; precipitation: mm; humidity: %; radiation: Langleys $min^{-1}$.

**TABLE 9.** Summary statistics of automated gaseous pollutant measurements and meteorological variables.* Sampling location: **Crossfield East.** Sampling period: 1985-1987. Time resolution of data: 1 hour.

| Variable | (n) | Mean | S.D. | Range | | Median | Percentile | | | | | | Skewness | Kurtosis |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Min. | Max. | | 10 | 30 | 70 | 90 | 95 | 99 | | |
| 1. $SO_2$ | 16436 | 1.3 | 4.2 | .00 | 92.3 | .40 | .30 | .40 | .50 | 1.9 | 5.8 | 20.4 | 8.8 | 108.9 |
| 2. $H_2S$ | 15713 | .33 | 1.2 | .00 | 49.3 | .10 | .00 | .10 | .20 | .30 | 1.3 | 5.5 | 12.1 | 269.9 |
| 3. NO | 16052 | 3.6 | 13.3 | .00 | 247.6 | .40 | .20 | .30 | .50 | 6.5 | 18.9 | 65.9 | 7.5 | 74.5 |
| 4. $NO_2$ | 16258 | 6.5 | 8.1 | .00 | 61.9 | 2.6 | 1.2 | 1.5 | 6.6 | 18.3 | 24.9 | 36.5 | 2.2 | 5.1 |
| 5. $CO_2$ | 16430 | 348.6 | 15.3 | 310.3 | 486.3 | 347.9 | 332.0 | 341.6 | 352.8 | 364.2 | 372.3 | 405.8 | 2.1 | 10.5 |
| 6. $O_3$ | 16566 | 24.7 | 13.0 | 1.9 | 73.8 | 25.0 | 5.5 | 17.5 | 31.7 | 41.1 | 46.8 | 56.5 | .19 | - .37 |
| 7. Wind Speed | 16735 | 12.7 | 9.4 | .00 | 70.4 | 11.0 | 1.9 | 7.0 | 16.0 | 25.4 | 30.3 | 41.6 | 1.1 | 1.8 |
| 8. Wind Direction | 16736 | 208.5 | 79.5 | 5.1 | 354.4 | 202.6 | 98.7 | 171.9 | 255.4 | 319.0 | 330.1 | 344.3 | - .25 | - .65 |
| 9. Temperature | 16384 | 5.3 | 9.7 | -31.20 | 30.8 | 5.8 | - 7.30 | .40 | 10.8 | 17.4 | 20.4 | 25.4 | - .33 | .10 |
| 10. Barometric Pressure | 16739 | 886.7 | 6.9 | 861.0 | 908.0 | 887.0 | 877.7 | 883.6 | 890.7 | 895.2 | 897.6 | 901.0 | - .31 | .12 |
| 11. Precipitation | 14752 | .001 | .01 | .00 | .60 | .00 | .00 | .00 | .00 | .00 | .00 | .00 | 17.8 | 536.9 |
| 12. Humidity | 15838 | 57.5 | 20.0 | 20.0 | 100.0 | 56.8 | 30.4 | 44.4 | 71.9 | 84.6 | 88.3 | 93.2 | - .02 | - 1.12 |
| 13. Radiation | 14844 | 348.8 | 485.9 | - 2.00 | 1935.3 | 64.0 | - 1.00 | .00 | 448.6 | 1167.1 | 1444.1 | 1739.6 | 1.4 | .71 |

* All gas concentrations in ppb, except $CO_2$ (ppm); wind speed: km $h^{-1}$; wind direction: degrees; temperature: °C; pressure: mbars; precipitation: mm; humidity: %; radiation: Langleys $min^{-1}$.

**TABLE 10.** Characteristics of highest mean hourly $O_3$ (ppb) at **Crossfield West** and **Crossfield East** on days identified as 'episode' or 'non-episode' at Fortress Mountain during 1987.*

| Crossfield West | | | | | | Crossfield East | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Episode | | | Non-Episode | | | Episode | | | Non-Episode | | |
| Date | Highest Hourly $O_3$ (ppb) | Hour | Date | Highest Hourly $O_3$ (ppb) | Hour | Date | Highest Hourly $O_3$ (ppb) | Hour | Date | Highest Hourly $O_3$ (ppb) | Hour |
| Apr 24 | 69.8 | 1800 | Apr 23 | 44.8 | 1100 | Apr 24 | 68.0 | 1800 | Apr 23 | 44.5 | 1100 |
| Apr 25 | 71.6 | 1400 | Apr 28 | 69.1 | 1400 | Apr 25 | 70.9 | 1400 | Apr 28 | 60.4 | 1400 |
| Apr 26 | 64.0 | 1400 | Apr 29 | 68.6 | 1300 | Apr 26 | 61.9 | 1500 | Apr 29 | 62.2 | 1800 |
| May 12 | 39.2 | 1200 | May 05 | 58.1 | 1500 | May 12 | 50.8 | 1600 | May 05 | 51.6 | 1500 |
| May 13 | 56.3 | 1800 | May 10 | 61.7 | 1500 | May 13 | 51.1 | 1800 | May 10 | 28.5 | 1800 |
| May 25 | 69.2 | 1700 | May 21 | 49.8 | 1200 | May 25 | 65.3 | 1700 | May 21 | 44.1 | 1100 |
| May 26 | 64.8 | 1300 | Jun 04 | 53.5 | 1700 | May 26 | 60.0 | 1700 | Jun 04 | 49.1 | 1300 |
| May 27 | 64.4 | 1500 | Jun 08 | 48.6 | 1600 | May 27 | 60.8 | 1700 | Jun 08 | 46.3 | 1600 |
| May 28 | 76.5 | 1400 | Jun 09 | 46.6 | 1600 | May 28 | 73.8 | 1400 | Jun 09 | 48.7 | 1500 |
| May 29 | 59.4 | 1400 | Jun 11 | 49.6 | 1700 | May 29 | 58.1 | 1400 | Jun 11 | 46.9 | 1700 |
| May 30 | 55.7 | 0900 | Jun 13 | 51.2 | 1600 | May 30 | 52.7 | 1600 | Jun 13 | 53.7 | 1600 |
| May 31 | 54.6 | 1600 | Jun 16 | 43.3 | 0100 | May 31 | 48.3 | 1500 | Jun 16 | 42.8 | 0100 |
| Jun 06 | 53.8 | 1800 | Jun 22 | 44.6 | 1100 | Jun 06 | 50.4 | 1900 | Jun 22 | 42.9 | 1100 |
| Jun 07 | 64.1 | 1600 | Jun 30 | 40.0 | 1700 | Jun 07 | 59.3 | 1600 | Jun 30 | 34.1 | 1700 |

* The episode and non-episode days are the same as those identified for **Fortress Mountain** (Table 3).

There was an increase in the primary pollutant concentrations (NO, $NO_2$) on episode versus non-episode days. However, the correlation coefficient between $NO_2$:NO versus $O_3$ concentrations was very poor (r 0.05) at **both Crossfield** sites. On episode days, mean wind speeds, temperature, and humidity were lower than on non-episode days. To the contrary, radiation on episode days was higher than on non-episode days. However, the correlation coefficients among these and other surface meteorological variables and $O_3$ were poor. No consistent pattern could be established between peak hourly $O_3$ concentration on episode or non-episode days and surface wind direction at either **Crossfield site.** Figures 11-13 show 3-dimensional plots of average hourly $O_3$ concentrations, as a function of hour of the day and month of the study, for the three sites. The episodic period during the Spring of 1987 is obvious, as is the diurnal course of the concentrations, even though both episode and non-episode days are represented in these monthly averages.

Based on the aforementioned considerations, **it appears highly probable that on episode days, $O_3$ in the air masses arriving at Fortress Mountain was subsequently carried aloft to the two Crossfield sites.** During the daytime vertical mixing, some portion of this $O_3$ was carried downwards, resulting in higher surface $O_3$ concentrations at the **Crossfield sites.**

Highest hourly $O_3$ concentrations on episode days at **Fortress Mountain** were observed near midnight (2300-2400 hours, Figure 4). This was followed by a steep decrease

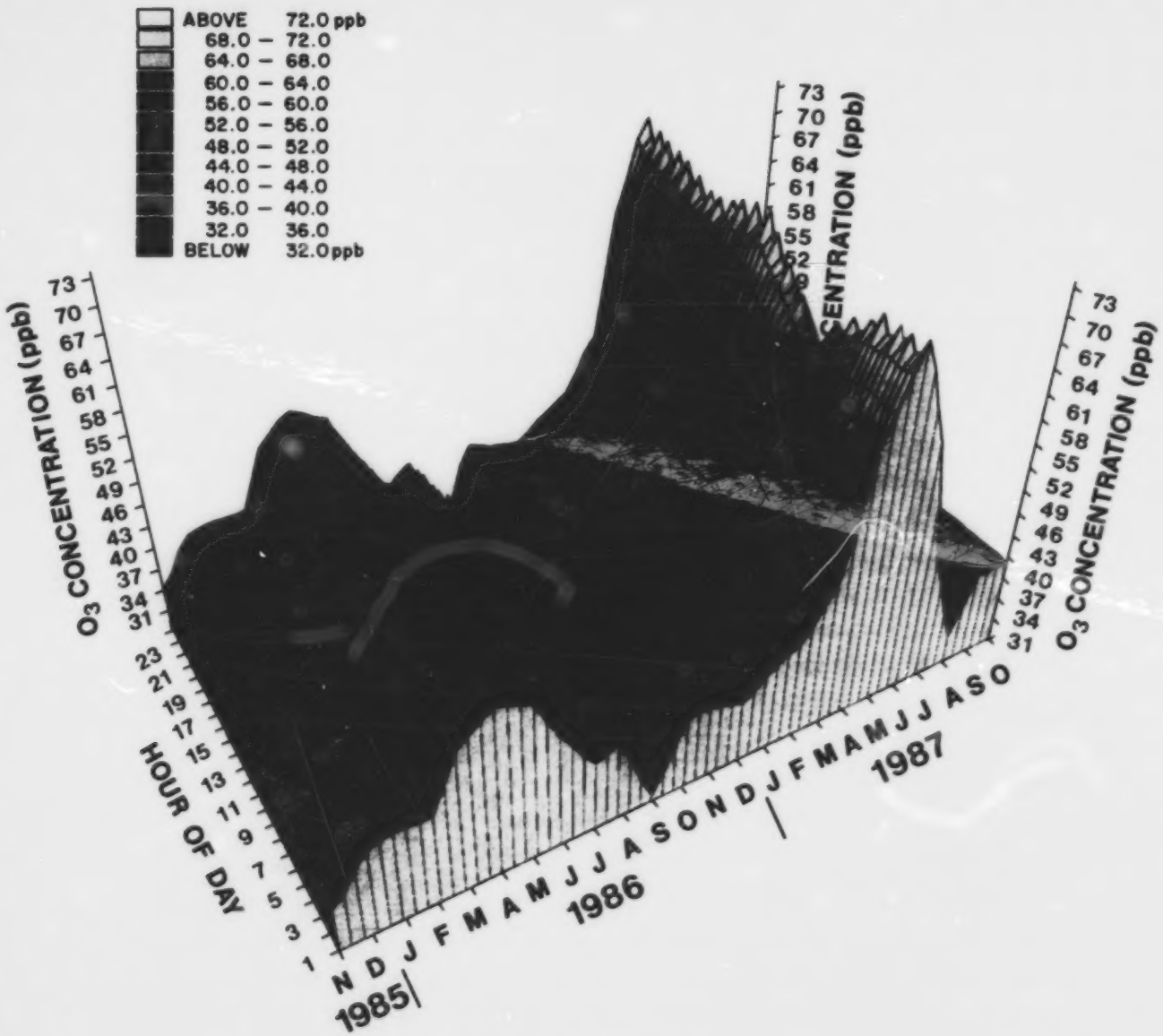


**Figure 11. Fortress Mountain**: Ozone concentration as a function of hour of the day and the month of the year (November 1, 1985 - October 31, 1987).

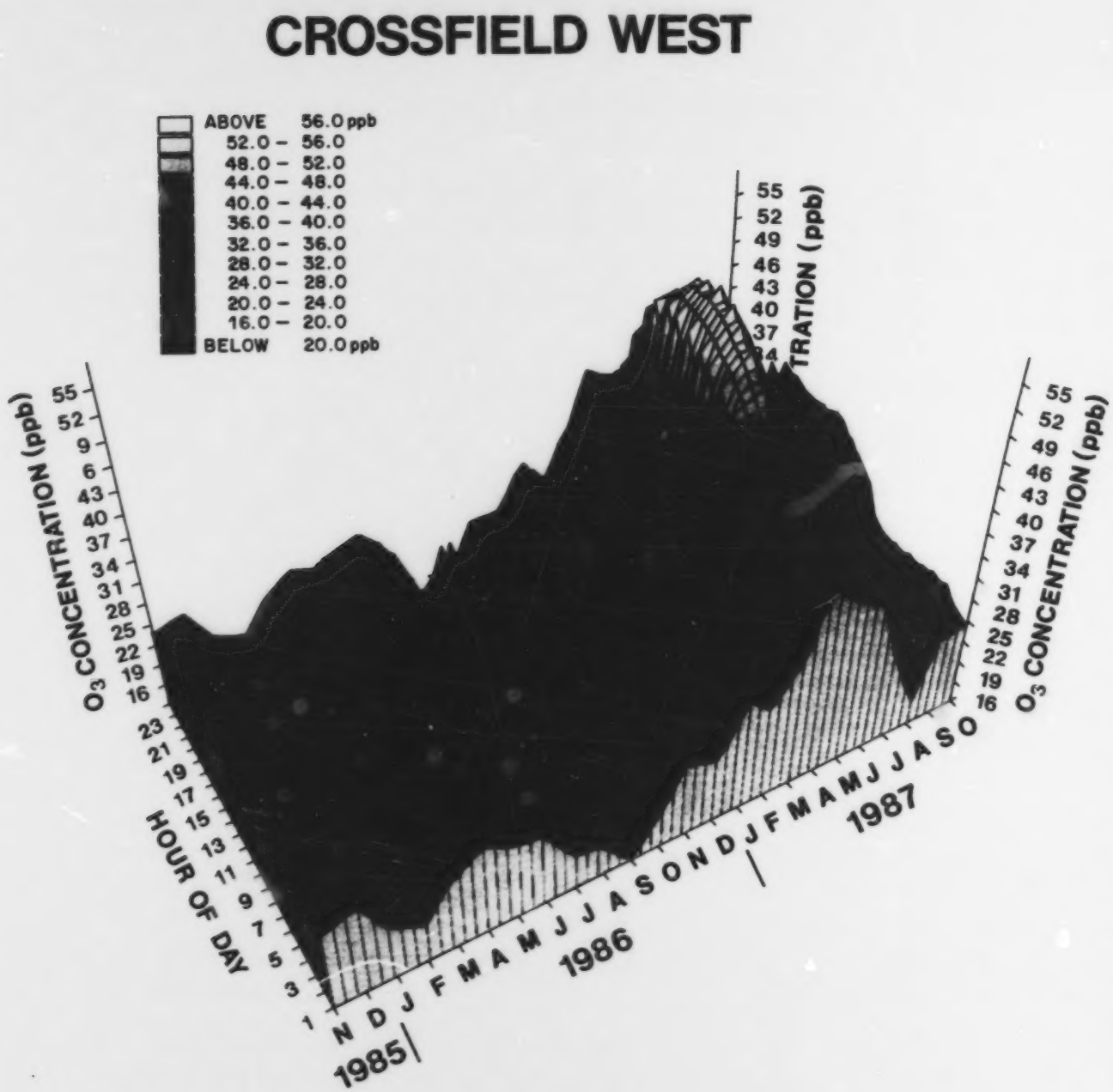


**Figure 12. Crossfield West:** Ozone concentration as a function of hour of the day and the month of the year (November 1, 1985 - October 31, 1987.

# CROSSFIELD EAST

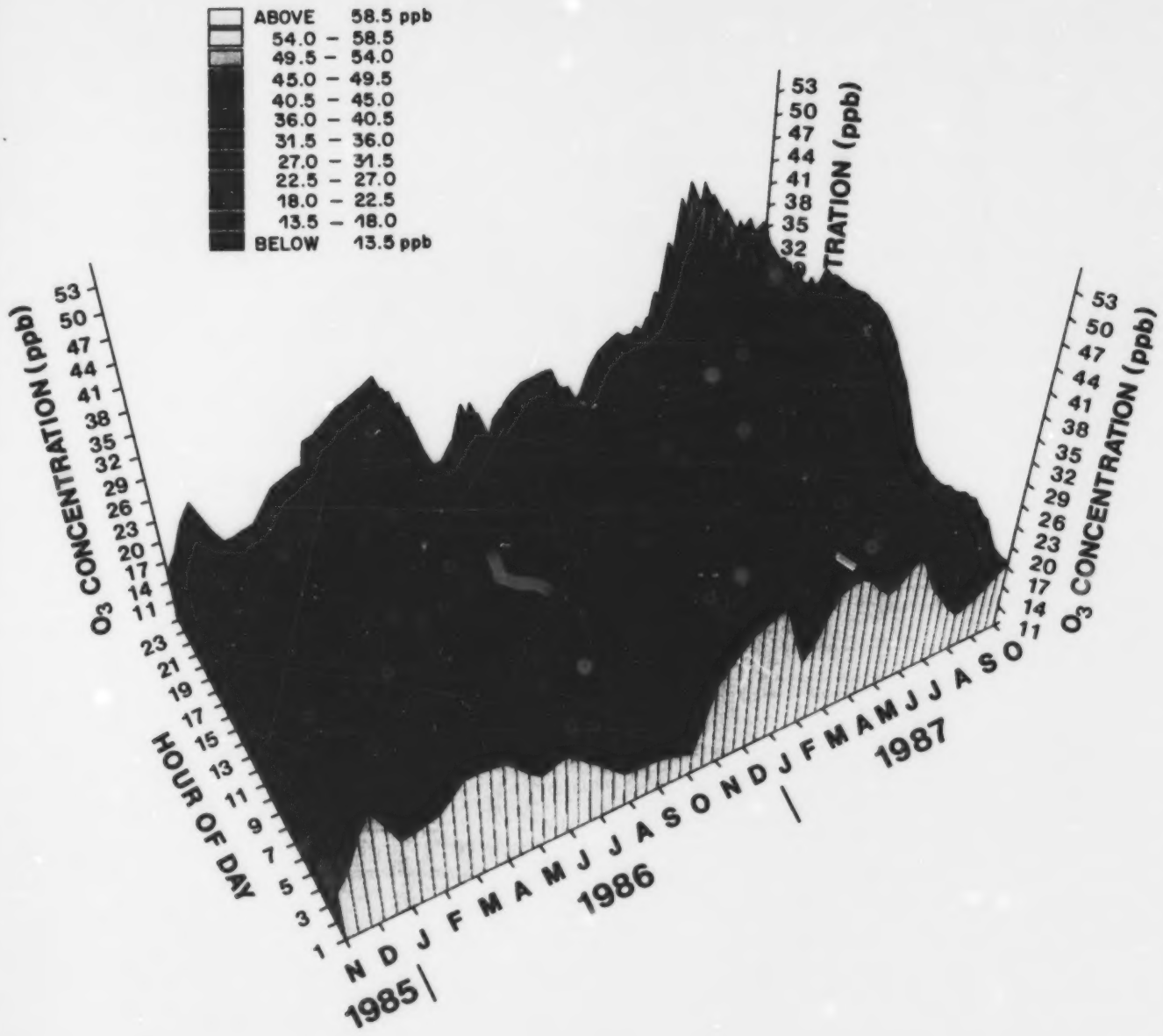


**Figure 13. Crossfield East:** Ozone concentration as a function of hour of the day and the month of the year (November 1, 1985 - October 31, 1987).

in hourly $O_3$ concentrations until 0800 hours after which concentrations increased again with a daytime peak at 1300 hours. In contrast, at the two **Crossfield sites**, the diurnal $O_3$ profiles were very similar to patterns typically observed at most monitoring sites (Figures 14 and 15). The $O_3$ concentrations increased from 0600 hours, reaching peak concentrations between 1500 and 1700 hours (2 hours after **Fortress Mountain**), and decreasing during the subsequent hours.

On episode days there was a clear, inverse relationship (r -0.94 to -0.96) between the late night (2400-0700 hours) decrease in the hourly $O_3$ concentrations at **Fortress Mountain** and mid-morning (0900 hours) rise in hourly $O_3$ concentrations at the **two Crossfield sites**. The r values for such a relationship on non-episode days were comparatively low (-0.42 to -0.56).

The **ratios** of hourly $O_3$ concentrations during 2400-0700 hours on **episode days** to the corresponding values on **non-episode days** at **Fortress Mountain** were well correlated to similar ratios on the same days but at 0900-1600 hours, at **both Crossfield West and Crossfield East** (r -0.84 and -0.91) respectively. Further, these episode:non-episode $O_3$ concentration ratios were also strongly correlated (r 0.94 between the **two Crossfield sites**). **Thus, the results obtained offer a strong argument for the transport of $O_3$ on episode days from the Fortress Mountain area to Crossfield.** This was further supported by the relative concentrations which, as previously noted, were highest at **Fortress** and lowest at **Crossfield East**.

Table 11 provides a comparative summary of the concentrations of four different sulphur gas species at the **two Crossfield sites**. These data were obtained by gas chromatography and should be considered as supplemental or additional information to the continuous monitoring. The objective of this work was to identify sulphur species other than $SO_2$ and $H_2S$ and to quantify concentrations of sulphur pollutants when they were present below the detection limits of the continuous measurement monitors. The mean and the range of concentrations of all four sulphur gases were higher at **Crossfield East** in comparison to **Crossfield West**, yet all these values were in the parts per billion range, considered to be very low based on published literature.

Background concentrations were often below the detection limits of the gas chromatograph with conventional sampling. To improve sensitivity a limited number of samples at the **Fortress Mountain** and **Crossfield West sites** were analyzed with cryogenic sampling. This research approach provided information on background concentrations of COS, $CS_2$, $H_2S$, and $SO_2$ (Table 12).

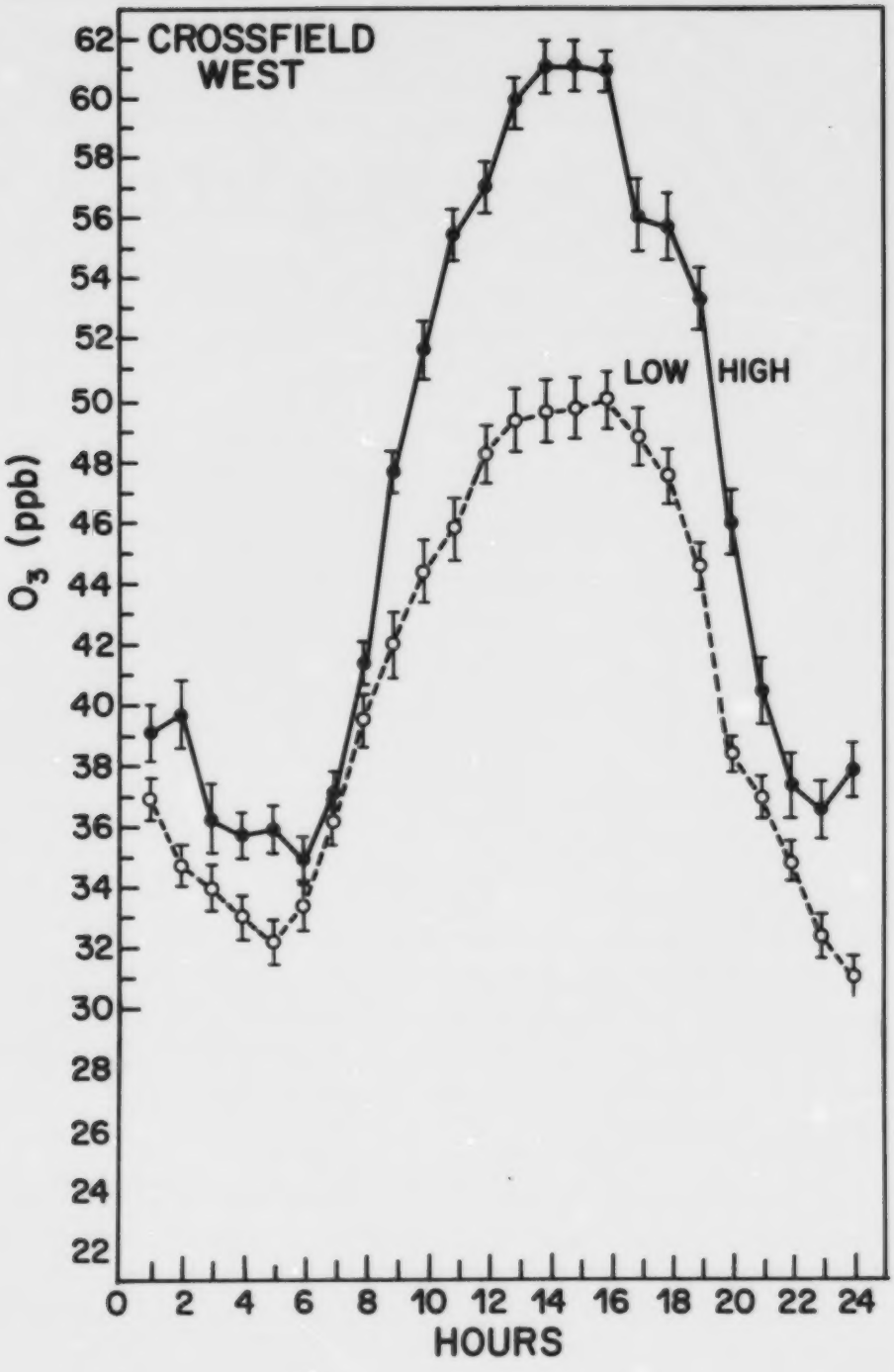


**Figure 14.** Diurnal $O_3$ profiles on episode (high) versus non-episode (low) days at Crossfield West The vertical bars represent S.D. of the mean for each hour.

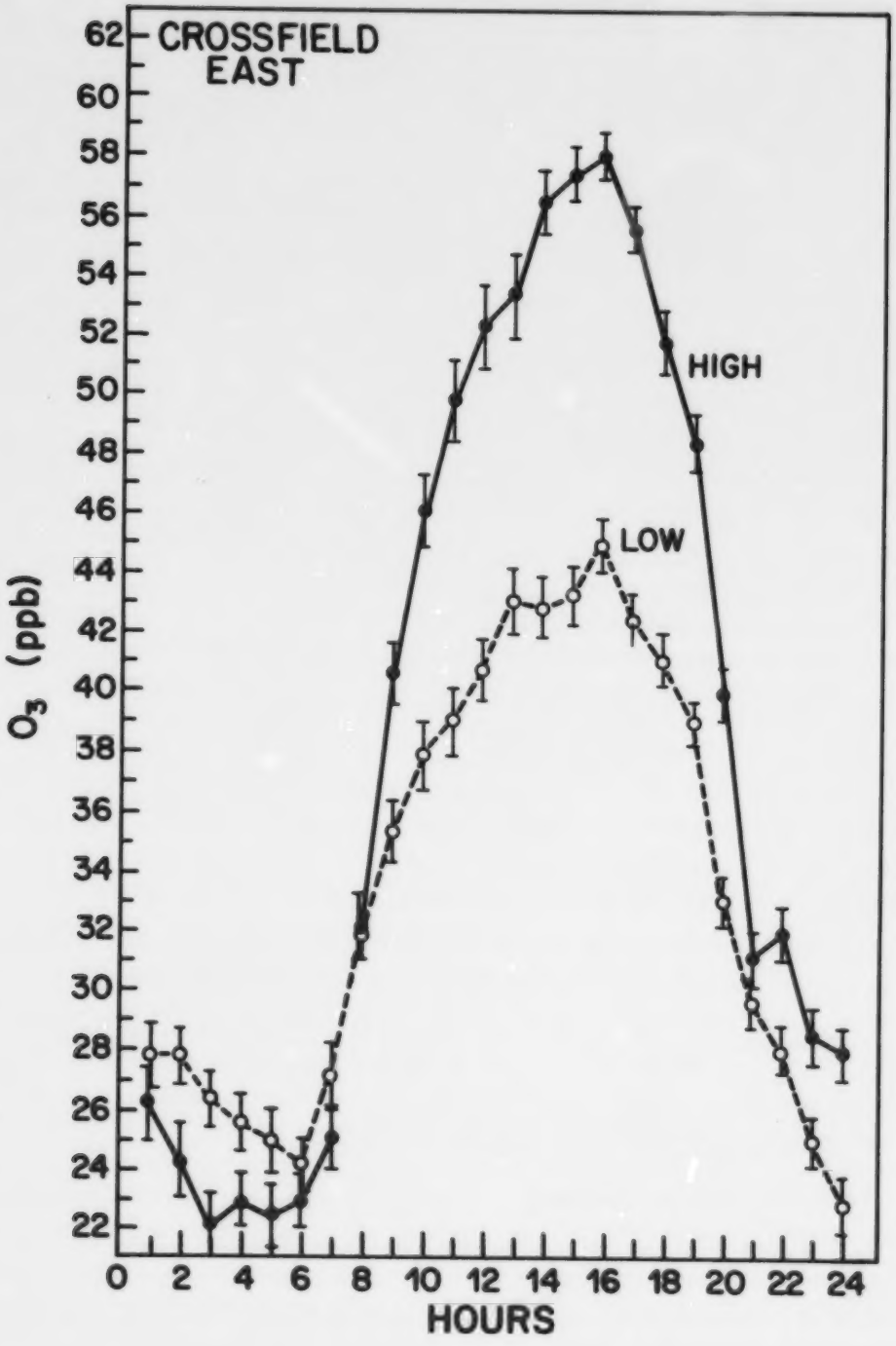


**Figure 15.** Diurnal $O_3$ profiles on episode (high) versus non-episode (low) days at Crossfield East The vertical bars represent S.D. of the mean for each hour.

**TABLE 11.** Summary statistics on the ambient concentrations of sulphur gases measured by conventional sampling and gas chromatography at Crossfield West and East (1985-87).

| | | Concentration (ppb) | | | | | |
|---|---|---|---|---|---|---|---|
| Pollutant | (n) | Mean | S.D. | Median | 75% | 99% | Range |
| **Crossfield West** | | | | | | | |
| COS | (2505) | 1.14 | 1.51 | 1.0 | 1.0 | 3.0 | 1.0-71 |
| $CS_2$ | (5285) | 1.22 | 1.20 | 1.0 | 1.0 | 7.0 | 1.0-28 |
| $H_2S$ | (8025) | 1.22 | 1.04 | 1.0 | 1.0 | 5.0 | 1.0-41 |
| $SO_2$ | (6183) | 2.14 | 3.66 | 1.0 | 1.0 | 2.0 | 1.0-82 |
| **Crossfield East** | | | | | | | |
| COS | (3051) | 1.73 | 1.82 | 1.0 | 2.0 | 9.0 | 1.0-33 |
| $CS_2$ | (7293) | 1.74 | 2.18 | 1.0 | 2.0 | 11.0 | 1.0-50 |
| $H_2S$ | (8373) | 2.56 | 4.02 | 1.0 | 2.0 | 21.0 | 1.0-57 |
| $SO_2$ | (16390) | 4.49 | 7.84 | 2.0 | 4.0 | 41.0 | 1.0-108 |

**TABLE 12.** Comparison of the mean and the range of sulphur gas concentrations measured by cryogenic sampling at Fortress Mountain and at Crossfield West.

| | Fortress Mountain | | Crossfield West | |
|---|---|---|---|---|
| Pollutant | Mean* | Range* | Mean* | Range* |
| COS | 0.32 | 0.23-0.42 | 0.24 | 0.18-0.35 |
| $CS_2$ | 0.018 | 0.01-0.03 | 0.02 | 0.007-0.06 |
| $H_2S$ | 0.07 | 0.04-0.10 | 0.07 | 0.03-1.20 |
| $SO_2$ | 0.53 | 0.25-0.96 | 1.40 | 0.37-5.60 |

* Concentration in ppb

The mean values of COS and $CS_2$ were higher at Fortress Mountain in comparison to Crossfield West. Values obtained at both sites were, however, within the range of background values reported in the literature (refer to Table 4). While the mean values for $H_2S$ were comparable at the two ADRP sites, the maximum concentration of $H_2S$ measured at Crossfield West was roughly 10 times the maximum concentration measured at Fortress Mountain. Similarly, the mean $SO_2$ concentration measured at Crossfield West was 259% higher than at Fortress Mountain, and the range was 146%-582% higher.

While at Fortress Mountain the r value between COS and $H_2S$ was 0.53, at Crossfield West these two variables were negatively correlated (r -0.10). $CS_2$ and $SO_2$ were negatively correlated (r -0.14) at Fortress Mountain but were positively correlated (r 0.45) at Crossfield West. These results suggest that the sources of COS, $H_2S$, $CS_2$, and $SO_2$ are different at the two monitoring sites.

At Fortress Mountain the similarity in the factor loadings of $CS_2$, COS, and $H_2S$ (Table 13) suggests the involvement of a common pathway of conversion of the three compounds and their possible origin from natural sources. Both $CS_2$ and COS are produced from oceans and soils and during biomass burning. In addition, the conversion of $CS_2$ to COS constitutes a major portion in the $CS_2$ flux.

**TABLE 13.** Comparison of the results of principal component analysis of the data from Fortress Mountain and Crossfield West.

| Variable | Factor Showing the Highest Value of Loading | |
|---|---|---|
| | Fortress Mountain | Crossfield West |
| COS | 1 | 2 |
| $H_2S$ | 1 | 1 |
| $CS_2$ | 1 | 1 |
| $SO_2$ | 2 | 1 |

$CS_2$, COS, $H_2S$, and $SO_2$ are also produced by anthropogenic activities (automobiles, fossil fuel combustion, wood pulping, and other industrial activities). The similarity in the loadings of $CS_2$, $H_2S$, and $SO_2$ at Crossfield West suggests an anthropogenic source(s) for these compounds. All three compounds are emitted during natural gas processing. Maximum concentrations of $CS_2$, $H_2S$, and $SO_2$ measured at Crossfield West were far higher than the corresponding values for Fortress Mountain. This was not true for COS (Table 12).

The range of concentrations of $SO_2$, $HNO_2$, $HNO_3$, $NH_3$, and fine particle (<2.5 μm) $NO_3^-$ and $SO_4^{2-}$ as measured by the serial annular denuder-filter pack system were higher at the two Crossfield sites in comparison to Fortress Mountain (Table 14). Similarly concentrations of coarse (>2.5 μm) particle crustal elements and fine (<2.5 μm) particle non-crustal elements were higher at the two Crossfield sites in comparison to Fortress Mountain (Table 15). All these findings support the conclusion that air quality at the Crossfield sites is affected by human activity far more than it is at the Fortress Mountain site.

**TABLE 14.** Comparison of concentration ranges of $SO_2$, $HNO_2$, $HNO_3$, $NH_3$, and fine particle $NO_3^-$ and $SO_4^{2-}$ at the three ADRP sites.

| Pollutant | Concentration range (μg $m^{-3}$) | | |
|---|---|---|---|
| | Fortress | Crossfield West | Crossfield East |
| $SO_2$ | 0.0003 - 16.9* | 0.002 - 23.6 | 0.002 - 22.0 |
| $HNO_2$ | 0.0005 - 0.46 | 0.003 - 2.3 | 0.003 - 2.1 |
| $HNO_3$ | 0.0005 - 3.4 | 0.003 - 2.1 | 0.003 - 3.7 |
| $NH_3$ | 0.04 - 1.3 | 0.22 - 12 | 0.24 - 8.3 |
| $NO_3^-$ | 0.02 - 0.66 | 0.05 - 5.8 | 0.05 - 9.8 |
| $SO_4^{2-}$ | 0.05 - 2.0 | 0.04 - 6.3 | 0.04 - 10 |

* At 25°C and 760 mm of Hg pressure, 2620 μg $m^{-3}$ $SO_2$ = 1 ppm.

**TABLE 15.** Ratio of selected coarse and fine particle elemental mean concentrations (ng $m^{-3}$) at the two Crossfield sites and at Fortress Mountain.

| Element* | Ratio Crossfield West: Fortress Mountain | Ratio Crossfield East: Fortress Mountain |
|---|---|---|
| Al (c) | 2.2 | 2.8 |
| Si (c) | 2.8 | 3.7 |
| Ca (c) | 3.7 | 4.7 |
| Mn (c) | 3.0 | 3.8 |
| Fe (c) | 2.6 | 3.4 |
| S (f) | 1.4 | 1.5 |
| Zn (f) | 1.7 | 2.0 |
| Se (f) | 2.7 | 2.9 |
| Br (f) | 1.8 | 4.4 |
| Pb (f) | 4.0 | 8.9 |

* c: coarse (>2.5 μm) and f: fine (<2.5 μm) particles.

**TABLE 16.** Median ion concentrations in rain: A comparison of data from the three ADRP sites with data from selected locations in Canada and the United States.

| Location | Range of Median Ion Concentrations (μg $L^{-1}$) | | | | |
|---|---|---|---|---|---|
| | $H^+$ | $SO_4^{2-}$ | $NO_3^-$ | $NH_4^+$ | $Ca^{2+}$ |
| **Fortress Mountain** | 0.013-0.019 | 0.67-1.18 | 0.55-0.80 | 0.16-0.49 | 0.60-0.65 |
| **Crossfield West** | 0.007-0.015 | 2.05-2.29 | 1.00-1.19 | 0.68-0.90 | 0.73-0.77 |
| **Crossfield East** | 0.009-0.015 | 2.83-3.58 | 1.31-1.48 | 0.65-0.86 | 0.83-1.46 |
| Bonner Lake, Ontario | 0.018-0.021 | 0.73-0.76 | 0.66-0.71 | 0.053-0.095 | 0.08-0.09 |
| Chalk River, Ontario | 0.052-0.063 | 1.67-2.05 | 2.04-2.17 | 0.194-0.302 | 0.09-0.11 |
| Cormack B, Newfoundland | 0.014-0.015 | 0.71-0.79 | 0.27-0.35 | 0.045-0.058 | 0.02-0.04 |
| Cree Lake, Saskatchewan | 0.011-0.015 | 0.43-0.49 | 0.18-0.40 | 0.053-0.058 | 0.03-0.04 |
| Island Lake, Manitoba | 0.009-0.011 | 0.43-0.46 | 0.35-0.53 | 0.084-0.087 | 0.07-0.08 |
| Montmorency, Quebec | 0.031-0.036 | 0.99-1.31 | 0.80-1.06 | 0.127-0.145 | 0.02-0.05 |
| Port Cartier, Quebec | 0.027-0.038 | 0.26-0.79 | 0.58-1.73 | 0.053-0.059 | 0.02-0.03 |
| Marcell, Minnesota | 0.003-0.006 | 0.95-1.01 | 1.30-1.53 | 0.170-0.200 | 0.17-0.22 |
| Hubbard Brook, New Hampshire | 0.041-0.046 | 1.73-1.77 | 1.28-1.40 | 0.120-0.130 | 0.04-0.08 |
| Whiteface Mountain, New York | 0.040-0.046 | 1.47-1.72 | 1.28-1.45 | 0.120-0.150 | 0.04-0.07 |
| Caldwell, Ohio | 0.076 | 3.20-2.87 | 1.89-2.07 | 0.230-0.340 | 0.17-0.18 |
| Leading Ridge, Pennsylvania | 0.056-0.076 | 2.53-3.16 | 1.75-2.43 | 0.230-0.350 | 0.10-0.14 |
| Olympic National Park, Washington | 0.004 | 0.24-0.32 | 0.01 | 0.010 | 0.03-0.05 |

Values for the Canadian monitoring sites are from the Environment Canada, Canadian Air and Precipitation Monitoring Network (CAPMoN).

Values for the U.S. monitoring sites are from the National Atmospheric Deposition Program (NADP).

In most cases, the values for 1985 and 1986 are used; ADRP values are for 1986 and 1987.

In comparison to **Fortress Mountain** (pH 4.77) the median pH values for daily rain at **Crossfield West** and **East** were 4.87 and 5.00, respectively. Table 16 shows median ion concentrations for the two years for all three ADRP sites in comparison with a number of sites in Canada and the U.S. **The Fortress Mountain site is clearly among the cleanest**; the

**Crossfield sites show the impact of regional (and perhaps local) sources.** Examination of correlations among the various ions shows a pattern similar to that at **Fortress Mountain**: stronger correlations of sulphate and nitrate with $NH_4^+$, $Ca^{2+}$, and $Mg^{2+}$ than with $H^+$. This finding is further strengthened by principal component analysis. At **Crossfield West**, Factor 1 contains $SO_4^{2-}$, $NO_3^-$, $Cl^-$, $Ca^{2+}$, $Mg^{2+}$, and $NH_4^+$, while Factor 2 is positively loaded for $Ca^{2+}$ and $Mg^{2+}$. At **Crossfield East**, Factor 1 is similar, but Factor 2 has a vanishingly small loading for $H^+$ and relatively low values for the alkaline earth elements. **A reasonable explanation is that the higher pH values at Crossfield result from progressive neutralization of the acidic species present by alkaline soil dust.**

Finally, examination of correlations between air chemistry and precipitation chemistry showed no strong relationships at **Crossfield**, in contrast to **Fortress Mountain**. This probably reflects the fact that **rain at Crossfield collects pollutants from a less homogeneous atmosphere**, so that surface measurements are less representative of the total air volume that affects the composition of the precipitation.

## 4. SOURCE APPORTIONMENT STUDIES NEAR CROSSFIELD

Once a large body of air monitoring data has been collected, it seems legitimate to ask: **What are the sources of the various pollutants?** In some cases, where a single enormous source is predominant, this question can be answered by simple inspection of the data. In addition, it was recognized many years ago that, on a gross level, some elements can be identified with particular types of sources—for example, vanadium with some types of petroleum and germanium with certain coals. However, particularly at very low levels of contamination, it is far more difficult to make this sort of assignment, since the soil itself is a source of nearly every element in the Periodic Table at some level or other.

Ultimately, a far more sophisticated technique was developed. To consider an extremely simple case, if there are two sources, one of which is characterized by emissions containing three times as much of element A as of element B, the other containing three times as much B as A, and if the air samples contain equal amounts of the two elements, then it is a reasonable conjecture that the two sources contribute equally to the pollutant complex that has been sampled. This can, of course, be greatly extended.

This approach requires the assumption that elements A and B are lost from the pollutant complex at equal rates. This will not be true, for example, if element A is associated with fine particles (<2.5 μm) which are removed from the air very slowly, and element B is associated with highly soluble gases or with coarse particles (>2.5 μm) which are removed far more rapidly.

This concept was developed into a technique called the **Chemical Mass Balance Method of Source Apportionment.** As many sources as possible are sampled, and the composition of their emissions analyzed. It is now customary to separate fine and coarse particles in this sampling, and to consider these fractions separately, improving the fit to the assumption noted previously. In some cases the sources may be so similar that they cannot be distinguished, and these are commonly lumped together. A group of elements which differentiates these sources as much as possible is selected. The elements selected are greater than the sources to be resolved. It is assumed that the composition of the air samples represents the sum of these contributions. Once this is stated mathematically, a series of simultaneous equations is obtained that may be solved by the method of least squares to yield the percentage contribution of each source. A system of solution is used that yields the best fit to these assumptions by some standard statistical test. The ultimate result is a statement of the most probable fractional contribution of each source to the ambient samples.

In the context of the **Crossfield sites**, there were a relatively small number of potential sources. Surrounding agriculture yielded soil dust and material from vegetation, whether the latter was generated by general decomposition or by combustion. The Crossfield sour gas plant yielded primarily gaseous pollutants, but accompanying particulate matter was also sampled from a number of the vents and chimneys. Dust was also raised from unpaved roads in the vicinity, and fine particulate matter was generated by both gasoline and diesel-powered vehicles. A final, important source that could not be characterized was the transport of particles from the Calgary Metropolitan area.

**Inspection of individual samples, allocated by wind direction, showed that sulphate and nitrate were high on days when the wind was from the Calgary area, and low on other days,** including days when either of the **Crossfield monitoring stations** was under the influence of the plume from the nearby sour gas plant. This is not unexpected; formation of sulphates and nitrates from sulphur and nitrogen oxides is a comparatively slow process and would not be expected to occur during the relatively short transport time from the gas plant to the monitoring sites.

The samples from the gas plant were collected simultaneously on both Teflon and quartz filters, and the latter used for separate analysis of organic compounds and soot. Unfortunately, similar parallel **ambient** sampling was not conducted at the **two Crossfield sites**; only Teflon filters were used, so organics and carbon could not be measured. As a result, the fraction of the collected particulate matter not explained by the calculations was large; it would be highly desirable to repeat these studies with added sampling and analytical capabilities.

Table 17 displays the mean values of the source apportionment for the two sampling sites over the entire period considered. **Roughly 40% of the fine particles were**

**TABLE 17. Crossfield East and Crossfield West:** Summary of average annual contributions of various sources to primary particle concentrations.

| Source | Fine | | Coarse | | Fine | | Coarse | |
|---|---|---|---|---|---|---|---|---|
| | $\mu g\ m^{-3}$ | Percent | $\mu g\ m^{-3}$ | Percent | $\mu g\ m^{-3}$ | Percent | $\mu g\ m^{-3}$ | Percent |
| | **Crossfield East** | | | | **Crossfield West** | | | |
| Soil and Road Dust | 0.90 | 12.75 | 8.52 | 45.81 | 0.51 | 11.02 | 4.16 | 78.20 |
| Vehicle Exhaust | 0.09 | 1.27 | 0.00 | 0.00 | 0.03 | 0.65 | 0.00 | 0.00 |
| Vegetation/Residue Burning | 0.59 | 8.36 | 0.56 | 3.01 | 0.58 | 12.53 | 0.26 | 4.89 |
| Ammonium Sulphate | 1.46 | 20.68 | 0.00 | 0.00 | 0.99 | 21.38 | 0.00 | 0.00 |
| Ammonium Nitrate | 0.99 | 14.02 | 0.00 | 0.00 | 0.61 | 13.17 | 0.00 | 0.00 |
| Sulphur | 0.12 | 1.70 | 0.03 | 0.16 | 0.08 | 1.73 | 0.02 | 0.38 |
| Other | 0.01 | 0.14 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Unexplained (Organics and Carbon?) | 2.90 | 41.08 | 9.49 | 51.02 | 1.83 | 39.52 | 0.88 | 16.54 |
| Mass | 7.06 | 100.00 | 18.60 | 100.00 | 4.63 | 100.00 | 5.32 | 100.00 |

**unexplained, and still more of the coarse particles at Crossfield East.** The apportionment at **Crossfield West** was more successful. **The strong dominance of the coarse particles by local soil and road dust (difficult to distinguish) is noteworthy.** In view of the relatively high pH of precipitation at these sites, all sulphate and nitrate was assumed to be in the form of the ammonium salts, and their strong contribution to the fine particle fraction is also worth noting. As previously remarked, these are characteristic of aged polluted air masses and arise primarily from air originating in the vicinity of Calgary. **The contribution of the local industry to particulate loadings is small.**

In summary, these samples are very typical of a fundamentally agricultural environment at a reasonable distance from a large city. More information could be gained by further sampling with additional sampling media and by continued analysis of the data already in hand.

## 5. WET AND DRY DEPOSITION OF AIR POLLUTANTS

With the exception of optical effects such as decreased visibility caused by airborne particles, air pollutants exert their effects only after they have been deposited, whether in human lungs or on plants, soils, or buildings. Thus, while it is useful to know airborne concentrations of these substances, the true measure of their possible impact can only be gained by determining their rates of deposition.

It is useful to consider two categories of deposition. Precipitation dissolves or includes airborne particles and soluble gases from the column of air in which the precipitating clouds form and through which the resulting rain or snow may pass, all in varying degrees. The resulting transport of airborne compounds to the underlying surfaces is **wet deposition**. In addition, gas molecules and fine particles diffuse to the surface, and large particles settle there. These, collectively, constitute the major components of **dry deposition**.

Wet deposition may be determined with some accuracy at a given site by collecting rainwater and analyzing it. Collection of snow is less satisfactory because no sampler yet devised will collect and retain snow during high winds, which frequently occur during snow storms. High winds also affect the collection of raindrops, but to a lesser degree since the terminal falling velocity of raindrops is markedly greater than that of snowflakes. By contrast, dry deposition is affected by numerous aerodynamic factors, as well as by the nature of the underlying surface. There exists no completely satisfactory technique for measuring dry deposition. The most widely applied approach is the estimation of a "**deposition velocity**". This may be thought of as the settling velocity of particles that are removed at the same rate as the pollutant under consideration, whatever its physical form. Thus, a deposition velocity may be computed for a gas such as $SO_2$, despite the fact that it does not settle under gravity.

Several experiments were conducted at the **Crossfield sites** to determine the deposition velocity of sulphur dioxide. **Mean values were in the vicinity of 0.7 cm sec$^{-1}$**. This value is comparable to measurements in other similar environments but higher than some estimates made for Eastern Canada. Published data on removal rates of fine particles vary, but coarse particle removal rates are well known.

Very complete data on the composition of rain were obtained at all three ADRP sites, together with measurements of precipitation amount. In addition, some data were available on the composition of individual samples of snow, and total snowfall depth and moisture content was also measured at or near all three sites. From these figures it was possible to make rather accurate estimates of wet deposition. As already noted, dry deposition cannot be measured with comparable confidence. However, knowing with some accuracy the concentrations of the various chemical species in the atmosphere, it was possible to estimate dry deposition, given a reasonable estimate of deposition velocity.

In this study, the Province of Alberta was divided into 10 regions for convenience of discussion. These are shown, together with the principal human settlements and highways, in Figure 16. Regions identified as having significant deposition of sulphur and nitrogen compounds were Regions 3, 4, 6, 7, and 9. Data on the composition of precipitation were available for one site in each of the first four of these, and at the **two Crossfield sites** in Region 9. The deposition rates were assumed representative of the respective regions. Comparable data on the composition of the atmosphere were not available in the first four regions but were estimated by suitable meteorological modelling, described in more detail in Section 7. From these estimated concentrations, dry deposition rates were computed by the same techniques used at Crossfield.

In addition, worst case scenarios were computed for all five regions, using measured or computed 90th percentile values of the concentrations; these were termed "maximum" deposition rates. The resulting values are displayed in Table 18.

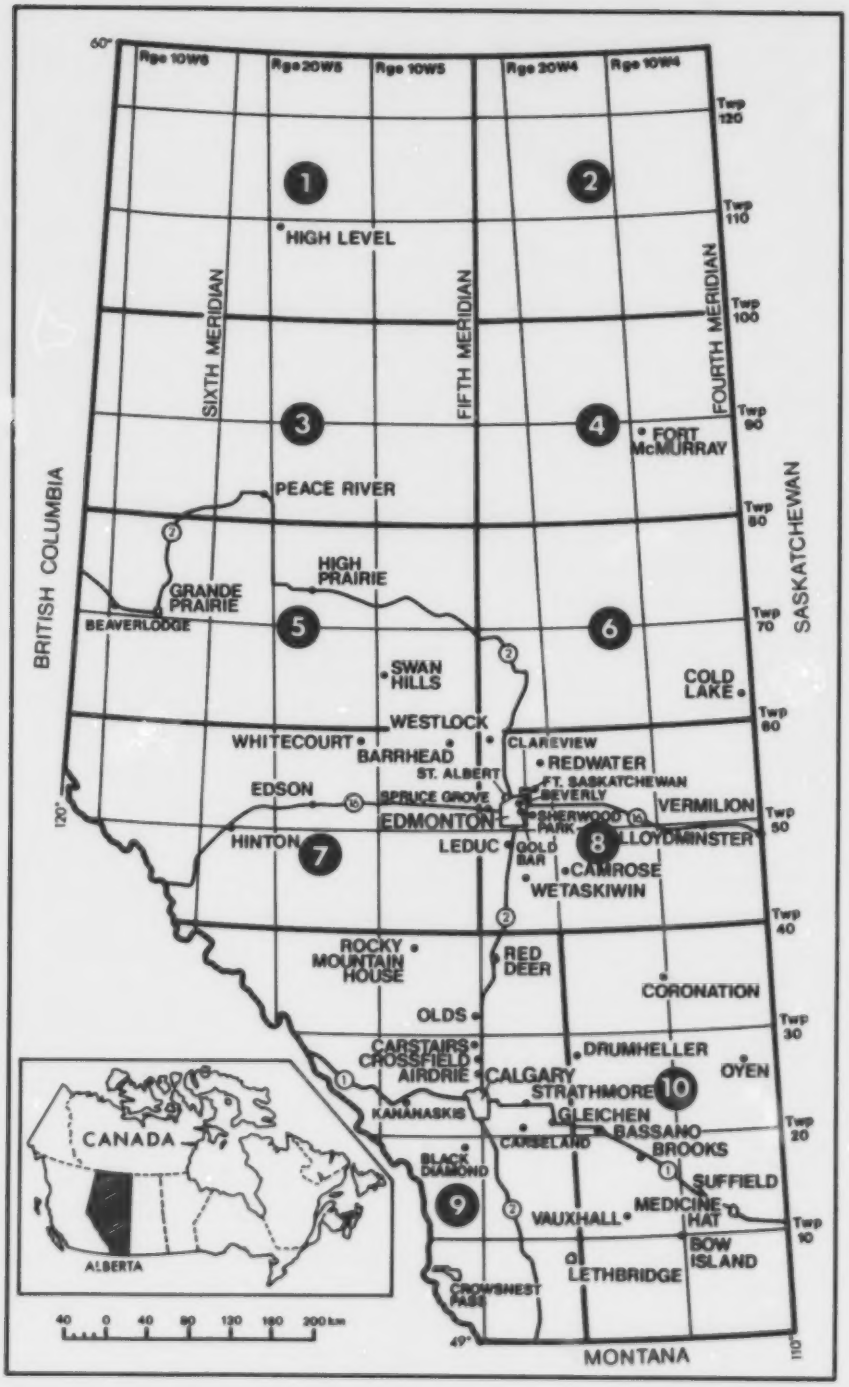


**Figure 16.** Map of Alberta showing major cities, and selected towns and villages, and three major highways (1, 2, and 16) with respect to geographic emission regions used in summarizing the $SO_2$ and $NO_x$ emissions data.

**TABLE 18.** Mean and 'maximum' values to be used in modelling of acidic deposition-ecological effects relationships (kg $ha^{-1}y^{-1}$).

| REGION 9 | Mean | | | Maximum | | |
|---|---|---|---|---|---|---|
| | Wet | Dry | Total | Wet | Dry | Total |
| $SO_4^{2-}$ | 10.8 | 14.2 | 25 | 26.8 | 27.4 | 54 |
| $NO_3^-$ | 5.6 | 5.7 | 11 | 15.1 | 20.9 | 36 |
| $Ca^{2+}$ | 2.8 | 1.9 | 4.7 | 5.4 | 7.8 | 13 |
| $Mg^{2+}$ | 0.45 | 0.29 | 0.74 | 0.98 | 1.05 | 2.0 |
| $Na^+$ | 0.51 | 0.14 | 0.65 | 1.34 | 0.12 | 1.6 |
| $K^+$ | 0.37 | 0.50 | 0.87 | 0.82 | 1.48 | 2.3 |
| $H^+$ | 0.090 | — | 0.090 | 0.28 | — | 0.28 |
| $NH_4^+$ | 2.4 | 4.1 | 6.5 | 9.6 | 17.6 | 27.2 |

Mean precipitation at Crossfield was 457 mm $y^{-1}$ and at Fortress Mountain 604 mm $y^{-1}$. The estimated mean for Region 9 was 506 mm $y^{-1}$.

Dry to wet ratio of $SO_4^{2-}$ at Crossfield was 1.48.

Estimated concentration of atmospheric particles was 30 μg $m^{-3}$.

Concentration of $NO_3^-$ in precipitation = 17 μmol $L^{-1}$.

Concentration of $NH_4^+$ in precipitation = 28 μmol $L^{-1}$.

Volume weighted pH was 4.79.

| REGION 3 | Mean | | | Maximum | | |
|---|---|---|---|---|---|---|
| | Wet | Dry | Total | Wet | Dry | Total |
| $SO_4^{2-}$ | 3.7 | 6.0 | 9.7 | 19 | 10 | 19 |
| $NO_3^-$ | 2.1 | 0.7 | 2.8 | 5.2 | 1.4 | 6.6 |
| $Ca^{2+}$ | 0.7 | — | — | 1.8 | — | — |
| $H^+$ | 0.036 | — | — | 0.09 | — | — |

Precipitation at Beaverlodge in 1986 was 463 mm.

Estimated concentration of atmospheric particles for Region 3 was 20 μg $m^{-3}$.

Concentration of $NO_3^-$ in precipitation = 7.3 μmol $L^{-1}$.

Concentration of $NH_4^+$ in precipitation = 8.7 μmol $L^{-1}$.

Volume weighted pH was 5.11.

| REGION 7 | Mean | | | Maximum | | |
|---|---|---|---|---|---|---|
| | Wet | Dry | Total | Wet | Dry | Total |
| $SO_4^{2-}$ | 10 | 12 | 22 | 25 | 18 | 43 |
| $NO_3^-$ | 4.3 | 3.2 | 7.5 | 11.6 | 9.7 | 21 |
| $Ca^{2+}$ | 5.3 | — | — | 14.3 | — | — |
| $H^+$ | 0.005 | — | — | 0.014 | — | — |

Precipitation at Edson in 1984 was 547 mm.

Estimated concentration of atmospheric particles for Region 7 was 25 μg $m^{-3}$.

Concentration of $NO_3^-$ in precipitation = 12.7 μmol $L^{-1}$

Concentration of $NH_4^+$ in precipitation = 11.3 μmol $L^{-1}$

Volume weighted pH was 6.02.

continued . . .

**TABLE 18.** (concluded)

| REGION 6 | Mean | | | Maximum | | |
|---|---|---|---|---|---|---|
| | Wet | Dry | Total | Wet | Dry | Total |
| $SO_4^{2-}$ | 2.5 | 7.6 | 10 | 6 | 12 | 18 |
| $NO_3^-$ | 1.0 | 2.7 | 3.7 | 2.6 | 5.5 | 8.1 |
| $Ca^{2+}$ | 1.1 | — | — | 3.0 | — | — |
| $H^+$ | 0.024 | — | — | 0.074 | — | — |

Precipitation at Cold Lake in 1986 was 417 mm.
Estimated concentration of atmospheric particles for Region 6 was 25 μg $m^{-3}$.
Concentration of $NO_3^-$ in precipitation = 3.7 μmol $L^{-1}$
Concentration of $NH_4^+$ in precipitation = 1.8 μmol $L^{-1}$
Volume weighted pH was 5.21.

| REGION 4 | Mean | | | Maximum | | |
|---|---|---|---|---|---|---|
| | Wet | Dry | Total | Wet | Dry | Total |
| $SO_4^{2-}$ | 9.6 | 11 | 21 | 24 | 42 | 66 |
| $NO_3^-$ | 1.8 | 0.7 | 2.5 | 4.5 | 2.8 | 7.2 |
| $Ca^{2+}$ | 5.4 | — | — | 15 | — | — |
| $H^+$ | 0.005 | — | — | 0.014 | — | — |

Precipitation at Fort McMurray in 1984 was 516 mm.
Estimated concentration of atmospheric particles for Region 4 was 20 μg $m^{-3}$.
Concentration of $NO_3^-$ in precipitation = 5.6 μmol $L^{-1}$
Concentration of $NH_4^+$ in precipitation = 1.2 μmol $L^{-1}$
Volume weighted pH was 6.01.

* Refer to Section 6 of this report for other details.

Deposition rates were also calculated at **Fortress Mountain** and were found to be markedly lower than those at the **Crossfield sites**. Sulphate deposition at Fortress Mountain was 40% of that at Crossfield, **the difference consisting largely of the dry deposition of** $SO_2$. **As previously noted, there is actually more initial acidity deposited at Fortress Mountain, because atmospheric free acids are neutralized by the alkaline soils at Crossfield.**

The deposition rates displayed in the table are comparable to estimates of similar environments elsewhere and are markedly below the maxima experienced in eastern Canada in highly industrialized regions such as southern **Ontario**. Estimated sulphate deposition in Region 9 (i.e., at Crossfield) was also accurately estimated by the same meteorological model used for the other regions. The model, however, somewhat under estimated the nitrate deposition. On the whole, however, these results gave added credibility to the modelling approach to be described later. **Throughout the Province, dry deposition was greater than wet deposition.**

## 6. ANTHROPOGENIC SOURCES OF ACIDIC AND ACIDIFYING AIR POLLUTANTS

As mentioned in the Introduction, one component of the ADRP study was a detailed inventory of emissions of sulphur and nitrogen oxides throughout Alberta, accurately identified as to location. Direct measurement of all emissions is, of course, impractical. Urban areas contain thousands of individual small sources, important only in aggregate. The same is generally true of highways as "line sources" of nitrogen oxides; obviously the highways do not emit such compounds, but the individual automobiles and other vehicles that traverse them do.

At one extreme, such an emission inventory can be entirely a "paper study" in which traffic data are compiled, industries are identified, and best guesses of the emissions of all sources are brought together based on emissions of similar industrial plants elsewhere in the world that have been measured. A slightly improved approach takes into consideration the actual production of the various industrial plants, and scales the emissions to the production figures. However, some industries may regard actual production levels as proprietary information and instead, quote total installed capacity or some other figure that may be only approximately related to the actual throughput of the operation. There are added complications; for example, the sulphur dioxide output of a coal-fired electricity generating plant depends not only on the sulphur content of the coal, but also on the composition of the ash, since highly alkaline ashes may retain as much as half of the coal sulphur.

The addition of pollution control equipment can further complicate the estimation of emissions. Faced with a legal requirement for example, of at least 95% control, an industry may elect to anticipate future tightening of the standards by purchasing equipment rated to remove at least 98%, and that equipment, depending on its maintenance and detailed design, may actually reduce emissions within a range of 95 to 99.5%.

The conclusion of this discussion is that for major sources, it is virtually indispensible to at least make direct measurements of emissions from typical sources using the fuels and raw materials available locally and customarily used. Extrapolation to even slightly dissimilar operations should be done with great caution. Similarly, nitrogen oxides emissions from vehicles is a fairly sensitive function of, among other things, altitude. Much of Alberta is at a significant height above sea level; therefore, typical U.S. test data originating near sea level can only be applied with major adjustments. It is preferable to substitute at least a few direct tests of representative vehicles at the altitude of Alberta, using fuels locally available. Similar considerations apply to many other types of provincial sources.

There is a final concern for completeness. Historically, there have been cases of major published emission inventories that completely omitted one or more large, conspicuous source facilities. Every effort has to be made, therefore, to insure that no major sources have

been omitted. At the same time, it is always necessary to pick some cutoff level below which emissions are judged insignificant. All of these factors were considered in the preparation of the most complete compilation, to date, of emissions within Alberta.

The need for these data is evident. As remarked in the previous section, for practical purposes in the present study, air quality data were obtained at only two locations, **Fortress Mountain** and **Crossfield**. The distribution of pollutants throughout the balance of the Province can only be determined by the use of suitable models, which require accurate information concerning the magnitude and location of added pollutants. The benefit of this excellent inventory was a remarkably accurate prediction of mean sulphur dioxide concentrations at the Crossfield sites, as noted previously.

The summary results of the inventory are given in Table 19 in comparison with a selection of states in the U.S. and provinces in Canada. Figure 17 shows graphically the magnitude of emissions of sulphur and nitrogen oxides from each of the regions identified in the previous section. A breakdown of source types by category is shown in Figures 18, 19, and 20. **It is clear that the major source of both pollutant types is the petroleum industry, followed by electric utilities, accounting together for almost two-thirds of the nitrogen oxides and over 98% of the sulphur oxides. The major sulphur dioxide emissions are shown to occur in Regions 4, 7, and 9, and the major emissions of nitrogen oxides are shown to occur in Regions 7, 8, 9, and 10.**

## 7. MODEL ESTIMATES OF PROVINCIAL-SCALE ATMOSPHERIC SULPHUR DIOXIDE AND OXIDES OF NITROGEN

The deposition (dry and wet) of airborne species provides an important input of acidic and acidifying substances into terrestrial and aquatic ecosystems. For a meaningful assessment of the importance of emissions, it is necessary to develop atmospheric models capable of predicting the deposition patterns resulting from the distribution of emission sources. Since the problems are regional in nature, it is necessary that these models be of regional extent in order to treat the processes occurring during long-range transport of the important species.

Models to simulate the distribution of pollutants in the atmosphere must include the consideration of three basic factors: the pollutant sources (the source inventory); atmospheric transport and diffusion (dispersion model); and pollutant decay (transformation and deposition). All air quality models include the first two components. Those involving purely local areas, where pollutant travel time from the source is less than several hours, often neglect the third. For regional and larger-scale models, all three components must be included.

**TABLE 19.** A comparison of annual $SO_2$ and $NO_x$ emissions in Alberta with the corresponding emissions in selected geographic locations in the U.S. and Canada.[1]

| Province or State | Annual Emissions (in 1000 Metric Tonnes) | | % A/B | |
|---|---|---|---|---|
| | $SO_2$ | $NO_x$ | $SO_2$ | $NO_x$ |
| Alberta (A) | 462.5 | 247.5 | | |
| Others (B) | | | | |
| Ohio | 2,401.1 | 1,038.4 | 19.3 | 23.8 |
| Indiana | 1,821.5 | 941.2 | 25.2 | 26.3 |
| Illinois | 1,334.1 | 912.0 | 34.7 | 27.1 |
| Mississippi | 1,180.4 | 258.8 | 39.2 | 95.6 |
| Texas | 1,158.2 | 2,307.7 | 40.0 | 10.7 |
| Kentucky | 1,016.7 | 482.0 | 45.5 | 51.3 |
| Washington | 246.7 | 262.1 | 187.5 | 94.4 |
| Montana | 148.6 | 114.0 | 311.2 | 217.1 |
| Ontario | 1,830.6 | 536.5 | 25.3 | 46.1 |
| Quebec | 1,157.9 | 331.4 | 39.9 | 74.7 |
| Manitoba | 489.9 | 78.1 | 94.4 | 316.9 |
| British Columbia | 192.9 | 199.0 | 239.8 | 124.4 |
| Saskatchewan | 57.8 | 148.3 | 800.2 | 166.9 |

[1] Source: For Alberta, Picard et al. (1987) Overview of the Emission Data: Emission Inventory of Sulphur Oxides and Nitrogen Oxides in Alberta. Acid Deposition Research Program, Calgary, Alberta, 87 pp; for others, United States-Canada Memorandum of Intent on Transboundary Air Pollution, Final Report, Work Group 3B (1982). Emission estimates for all geographic areas (other than Alberta) were for 1980.

It was decided at an early date that no attempt would be made to model short-term fluctuations in pollutant concentrations, but rather to seek a statistical model that could reasonably simulate seasonal and annual mean concentrations. Thus the search was limited to statistical models that treated long-term average meteorological and emission conditions. The model ultimately selected was the Climatological Dispersion Model (CDM), originally developed by the U.S. Environmental Protection Agency for treating air quality in large urban areas. It was subsequently modified (CDMW) by the Wyoming Department of Environmental Quality for application to rural areas. It was further modified for purposes of the present study by increasing the distance and time steps to match the scale of the entire Province. The basic unit of the model assumes that pollutants from individual sources diffuse in the atmosphere in a Gaussian fashion; that is to say, the concentration profile from a given source on a line perpendicular to the wind direction resembles a normal probability curve, and can be represented by a relatively simple exponential function of distance from the plume centreline.

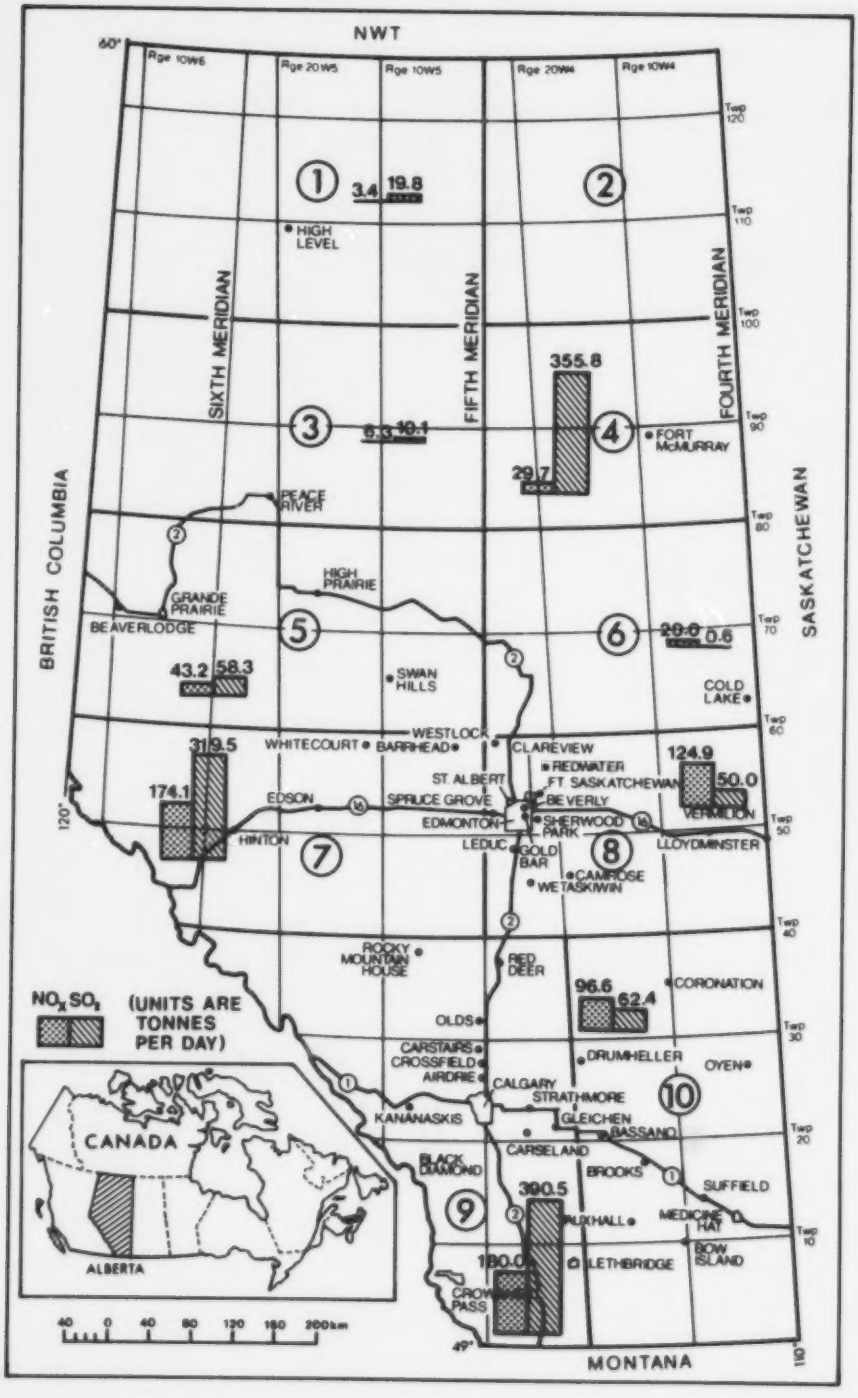


**Figure 17.** Map of Alberta showing total $NO_x$ and total $SO_2$ emissions as histograms in each of the 10 geographic emission regions.

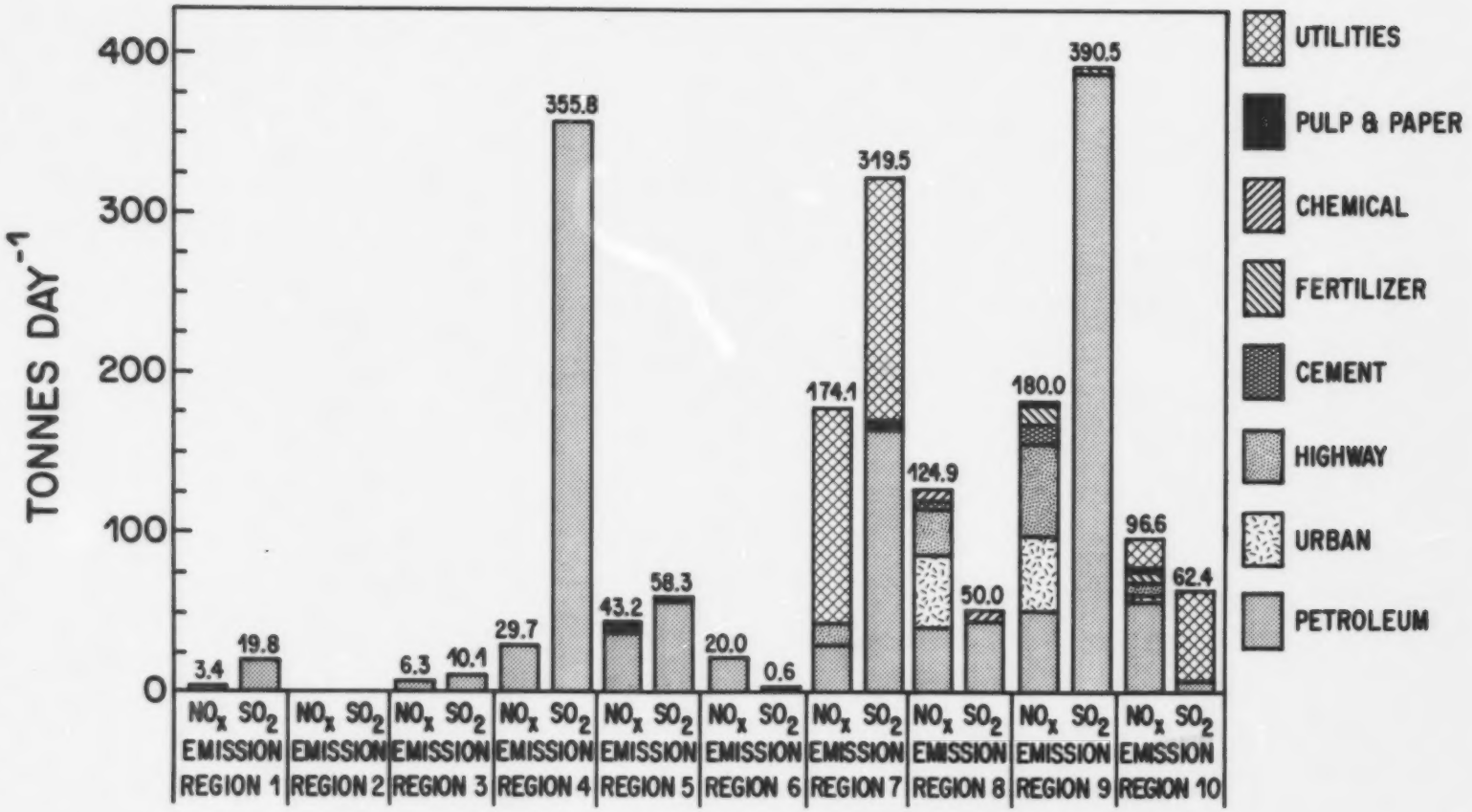


**Figure 18.** Total $NO_x$ and total $SO_2$ emissions by source category for each geographic emission region.

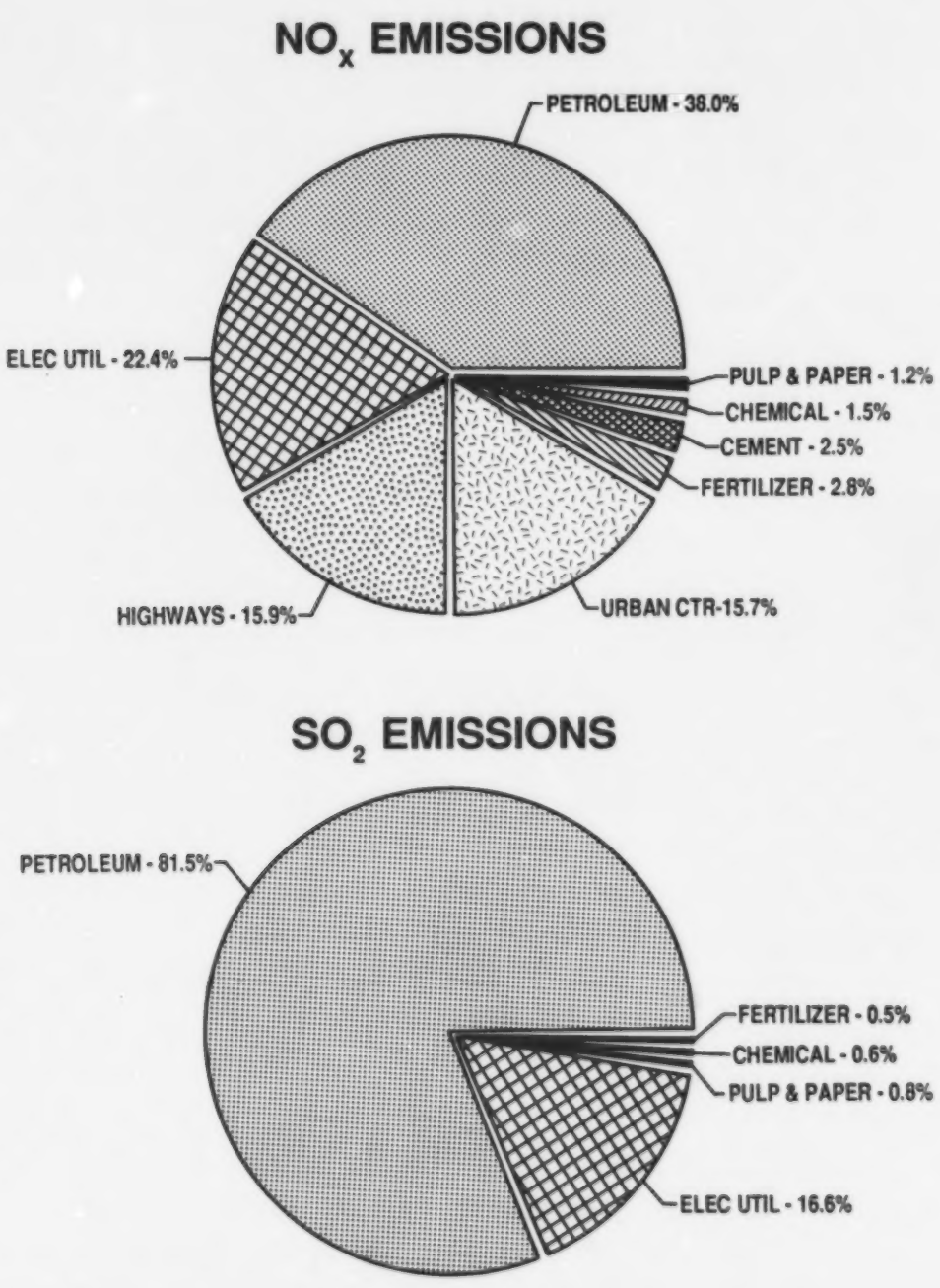


**Figure 19.** Total $NO_x$ and total $SO_2$ emissions as a function of the percentage contribution by each major source category in Alberta.

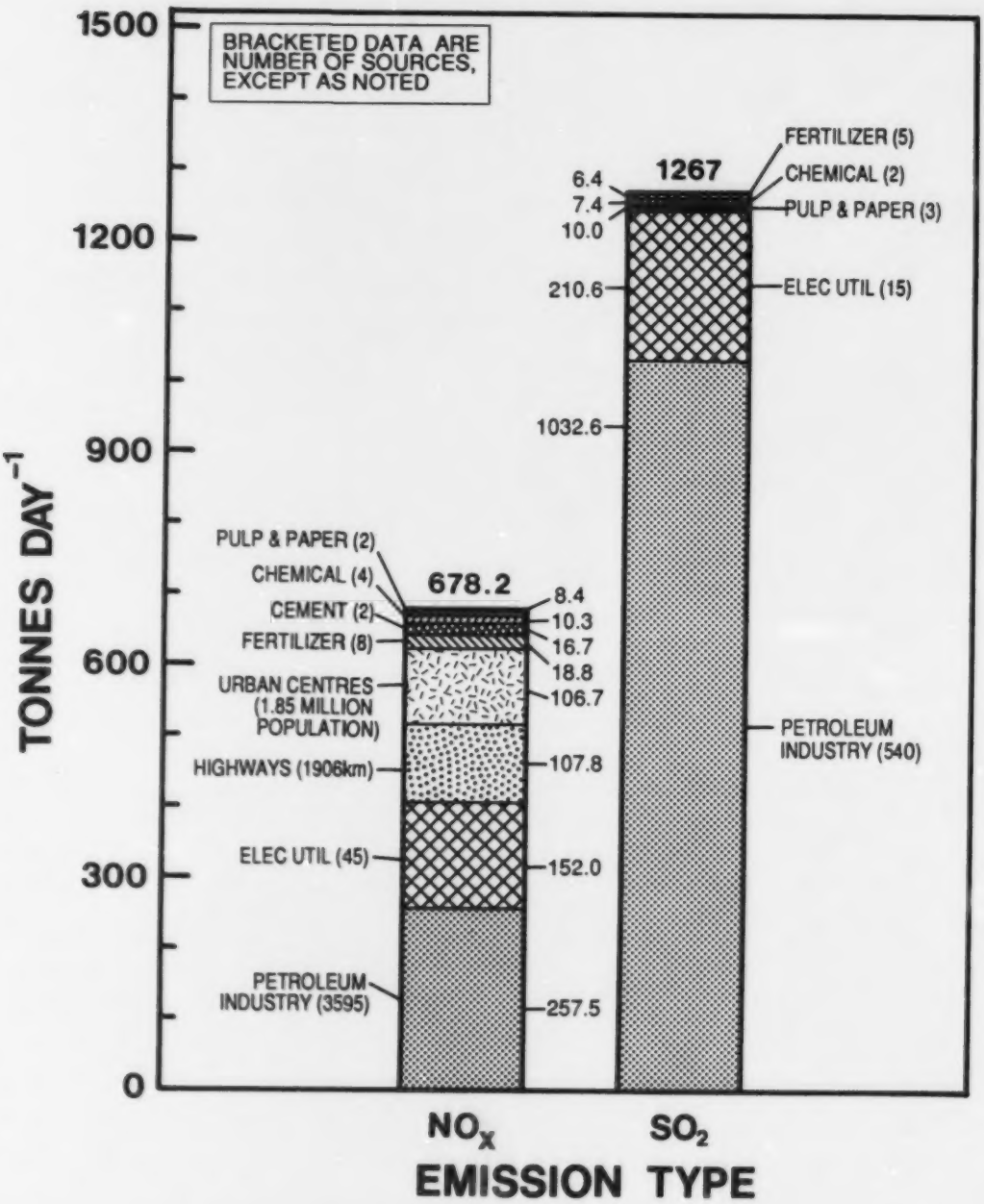


**Figure 20.** Total $NO_x$ and total $SO_2$ emissions in Alberta by major source category.

The emission inventory described in the previous section includes 565 individual sources of $SO_2$ and 4025 sources of $NO_x$. Individual major sources (annual average emission rate greater than 1 tonne $day^{-1}$) were represented in the model as point sources at their true location. All smaller sources were combined within their appropriate locations in a grid of 20 km x 20 km squares covering the Province, and were treated as area sources. This combination reduced the number of individual sources to a more manageable level of 78 point sources and 659 area sources. Climatological data on average seasonal and annual temperatures and mixing depths were obtained, as were values of the frequency of various classes of atmospheric stability, wind direction, and wind speed. Literature study and contact with experts extracted reasonable values of the transformation rates of the various pollutants, and the best estimate was made of the average lengths of periods of precipitation and of dry weather. All these data provided input to the resulting models. In each case, both seasonal (winter/summer) and annual average values were obtained. Where necessary, different transformation rates were assumed during wet and dry periods. Background concentrations were determined from the data from **Fortress Mountain**, and from comparison with measurements made elsewhere.

The model used all these data to calculate separately the contributions at each location from each point and area source and, for each location, the sum corrected for removal.

**Computed annual mean contours of concentrations of $SO_2$, $NO_x$, and $SO_4^{2-}$ are shown in Figures 21-23. The model concentrations appear reasonable, but there are few data against which to check them.** Annular denuder-filter pack measurements at **Crossfield** and **Fortress Mountain** are compared with the model data in Table 20. The annular denuder did not measure nitrogen oxides. However, the corrected data from the continuous monitors at **Crossfield** suggest annual average concentrations in the range of 6 to 20 $\mu g\ m^{-3}$. Short-range, and hence more proven, models yielding $SO_2$ concentrations in the range of 10 to 15 $\mu g\ m^{-3}$, are in reasonable agreement with the present modelling results.

Once a pollutant transport model is developed and found to yield credible results, one of the major uses has been the investigation of the effect of changes in source location and/or magnitude. A model can thus be used to study the impact of added sources, or the consequences of varying degrees of control of all or some of the existing sources.

One scenario was developed in which total provincial emissions of sulphur dioxide were increased by 16%, and nitrogen oxides by about 2.5%. The actual locations and source strengths used are shown in Table 21. The results are shown graphically in Figures 24, 25, and 26. These are to be compared with Figures 21, 22, and 23. As can be easily seen, the impact of this much change is small, except in the immediate vicinity of the sources.

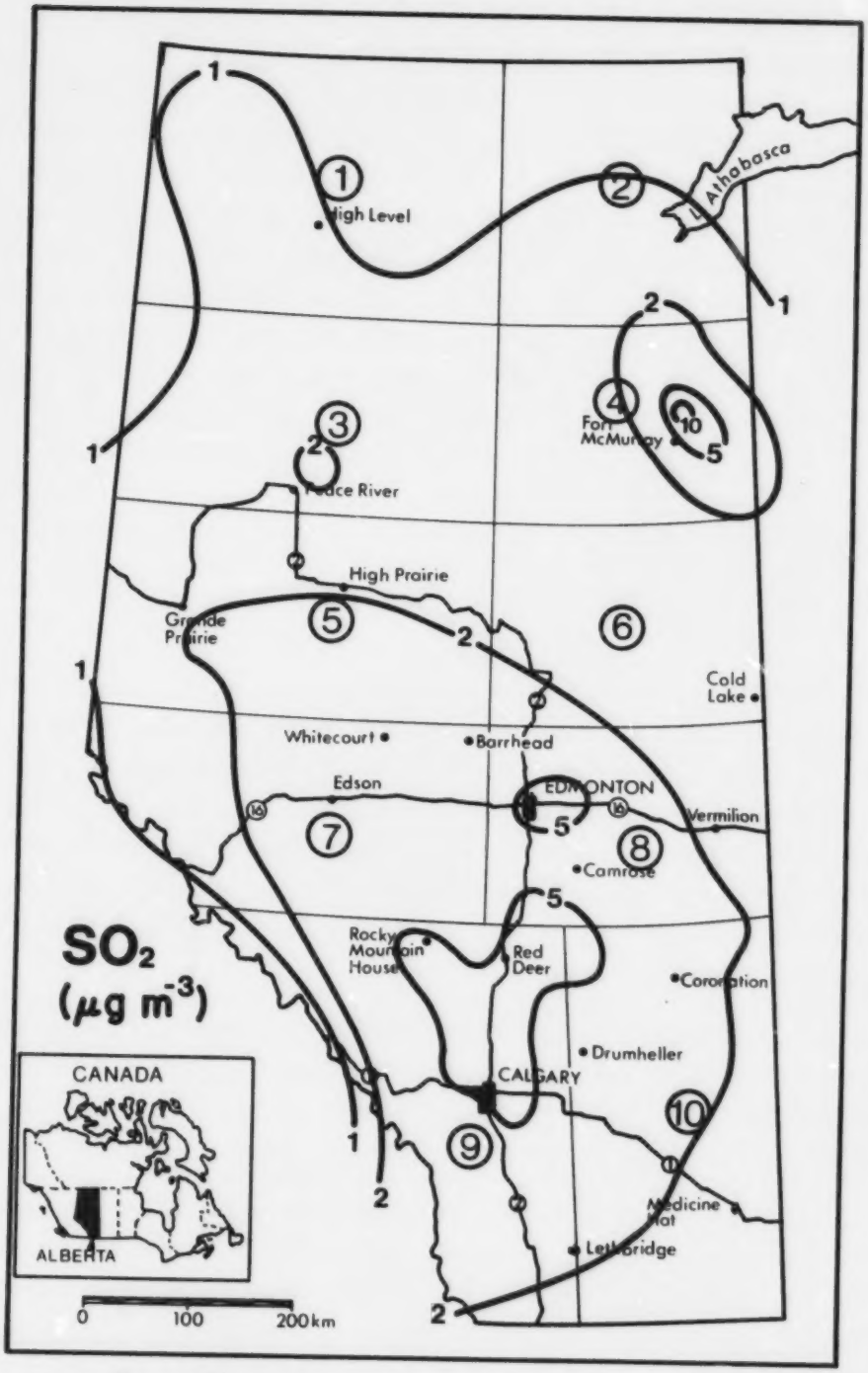


**Figure 21.** Average annual $SO_2$ concentration ($\mu g\ m^{-3}$).

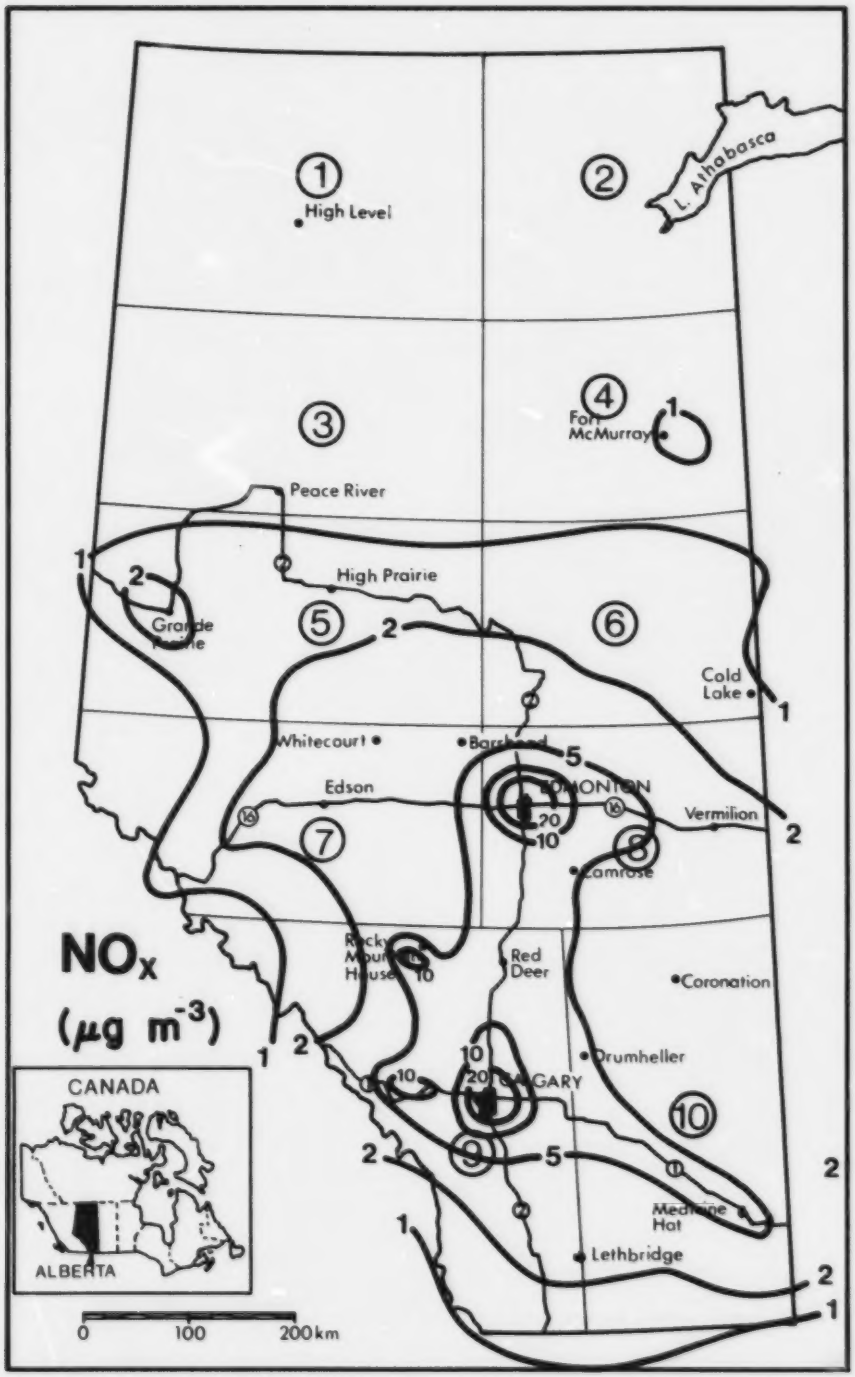


**Figure 22.** Average annual $NO_x$ concentration ($\mu g\ m^{-3}$).

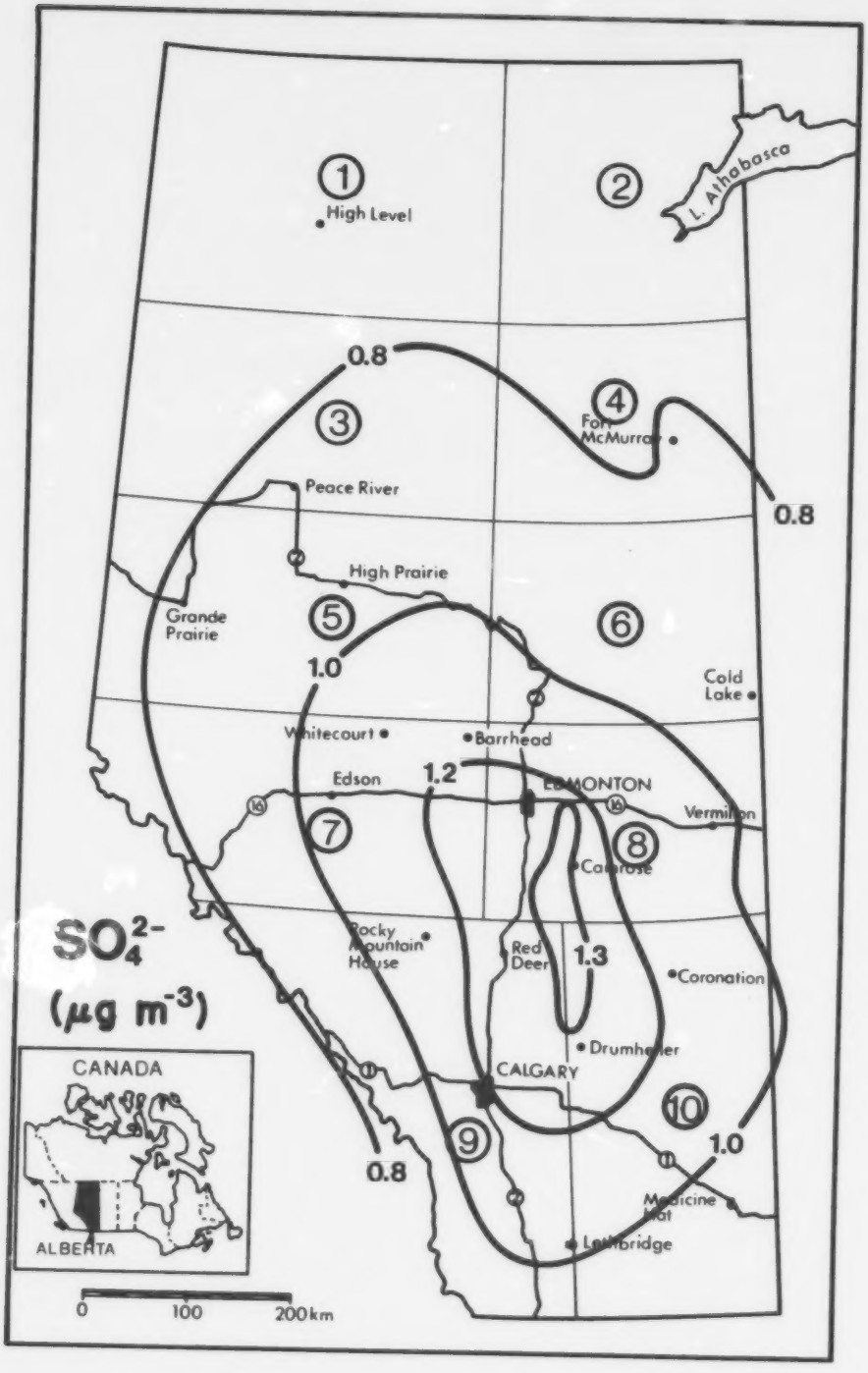


**Figure 23.** Average annual $SO_4^{2-}$ concentration ($\mu g\ m^{-3}$).

**TABLE 20.** Comparison of two independent methods for estimating atmospheric concentrations of $SO_x$ and $NO_x$ ($\mu g\ m^{-3}$).

| | Site Specific KAPS | Regional Model |
|---|---|---|
| **Crossfield East** | | |
| $SO_2$ | 4.8 | 6.5 |
| $SO_4^{2-}$ | 1.0 | 1.2 |
| $NO_x$ | — | 15.0 |
| **Crossfield West** | | |
| $SO_2$ | 3.9 | 6.5 |
| $SO_4^{2-}$ | 0.9 | 1.2 |
| $NO_x$ | — | 15.0 |
| **Fortress Mountain** | | |
| $SO_2$ | 0.9 | 2.5 |
| $SO_4^{2-}$ | 0.4 | 0.9 |
| $NO_x$ | — | 5.0 |

KAPS = Integrated annular denuder-filter pack measurement; sampling duration, **Fortress Mountain**: 48 h; **Crossfield (East and West)**: 24 h.

**TABLE 21.** Hypothetical emission sources assumed for future scenario in Alberta.

| Location | Number of Sources | $SO_2$ Emission ($t\ d^{-1}$) | $NO_x$ Emission ($t\ d^{-1}$) |
|---|---|---|---|
| Peace River | 1 | 14.0 | 0.0 |
| Oil Sands (Fort McMurray) | 2 | 64.6 | 13.2 |
| Cold Lake | 1 | 38.9 | 0.9 |
| Caroline | 1 | 42.7 | 0.0 |
| Sundre | 1 | 42.7 | 0.0 |

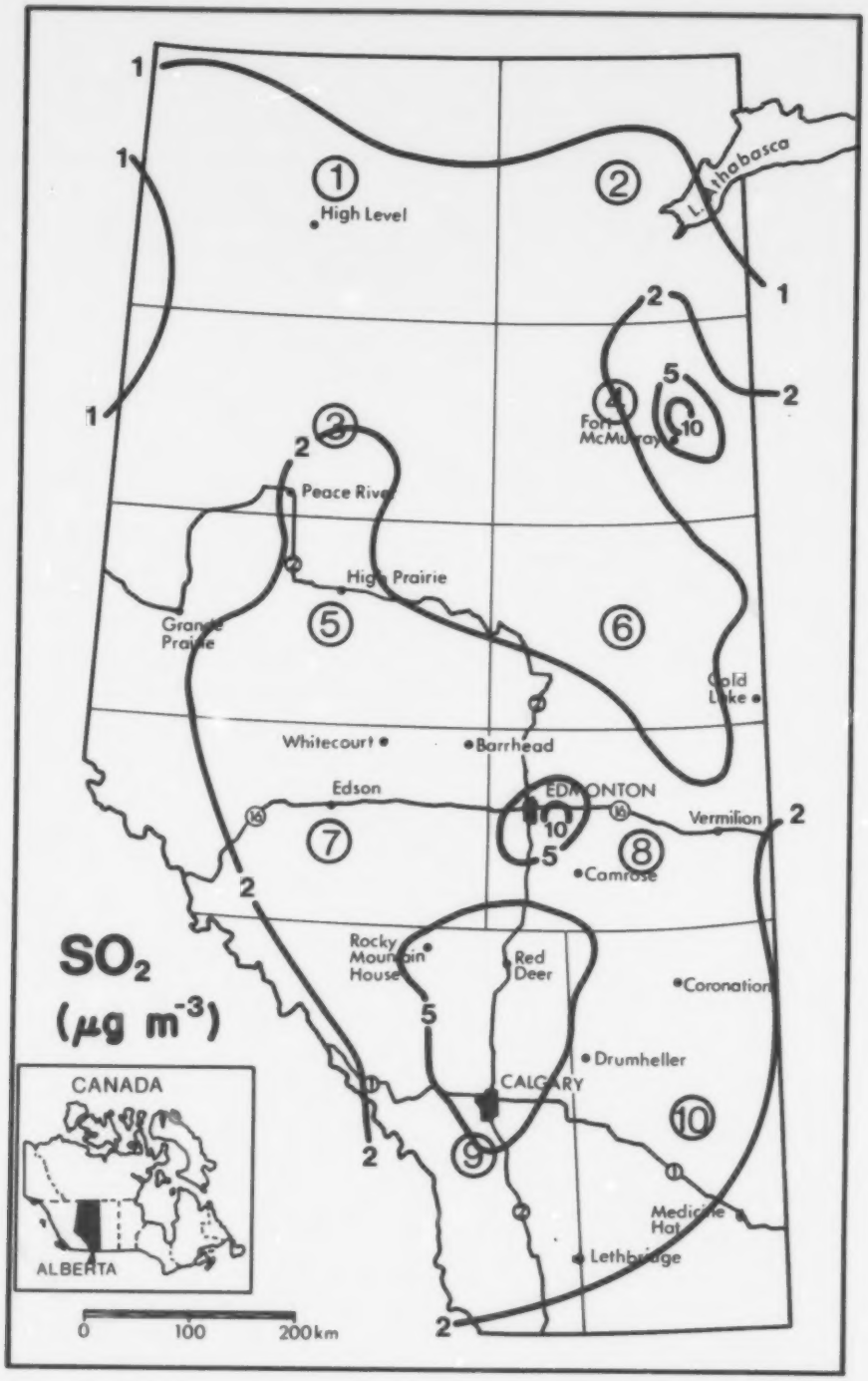


**Figure 24.** Average annual $SO_2$ concentrations - future scenario ($\mu g\ m^{-3}$).

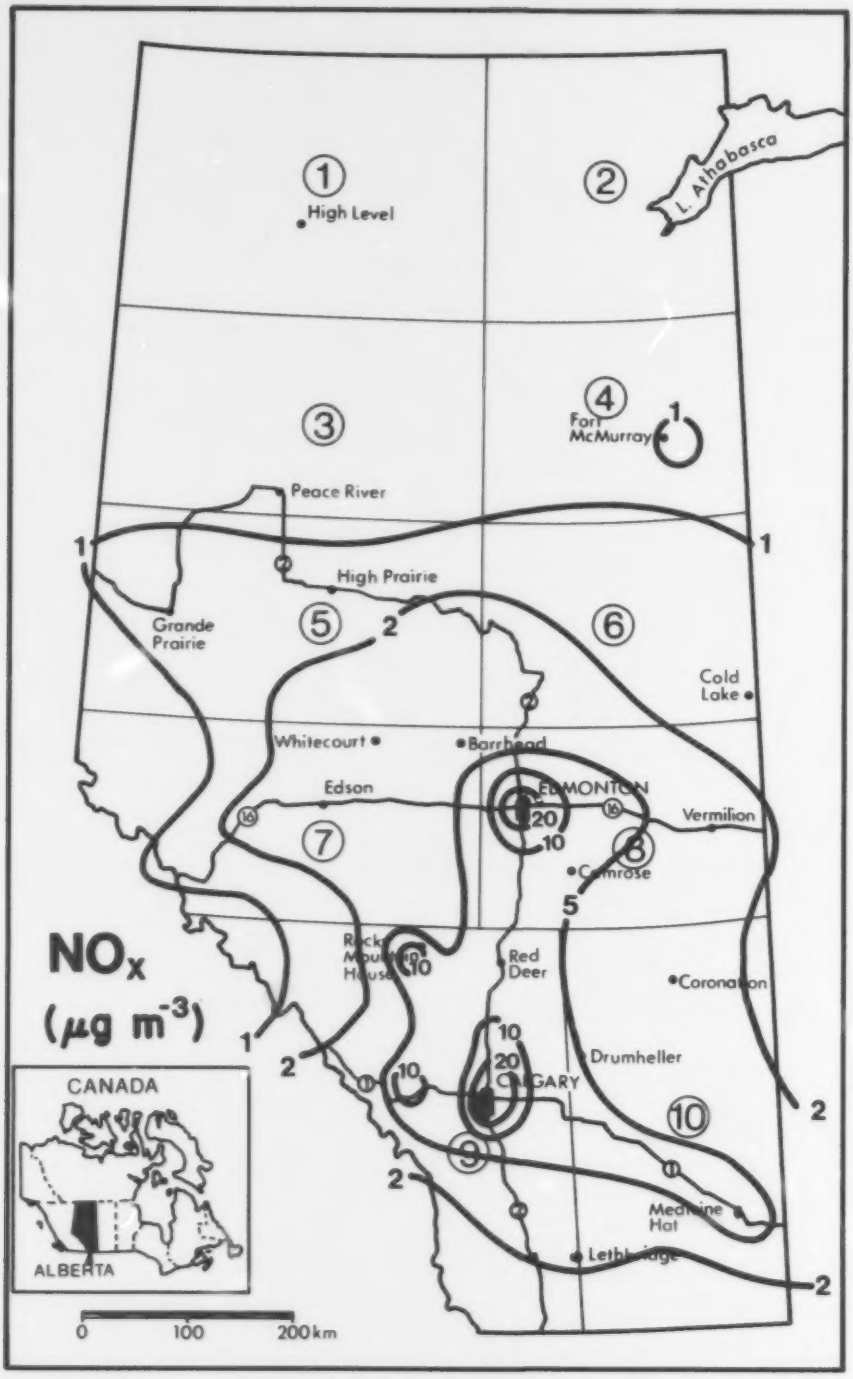


**Figure 25.** Average annual $NO_x$ concentrations - future scenario ($\mu g\ m^{-3}$).

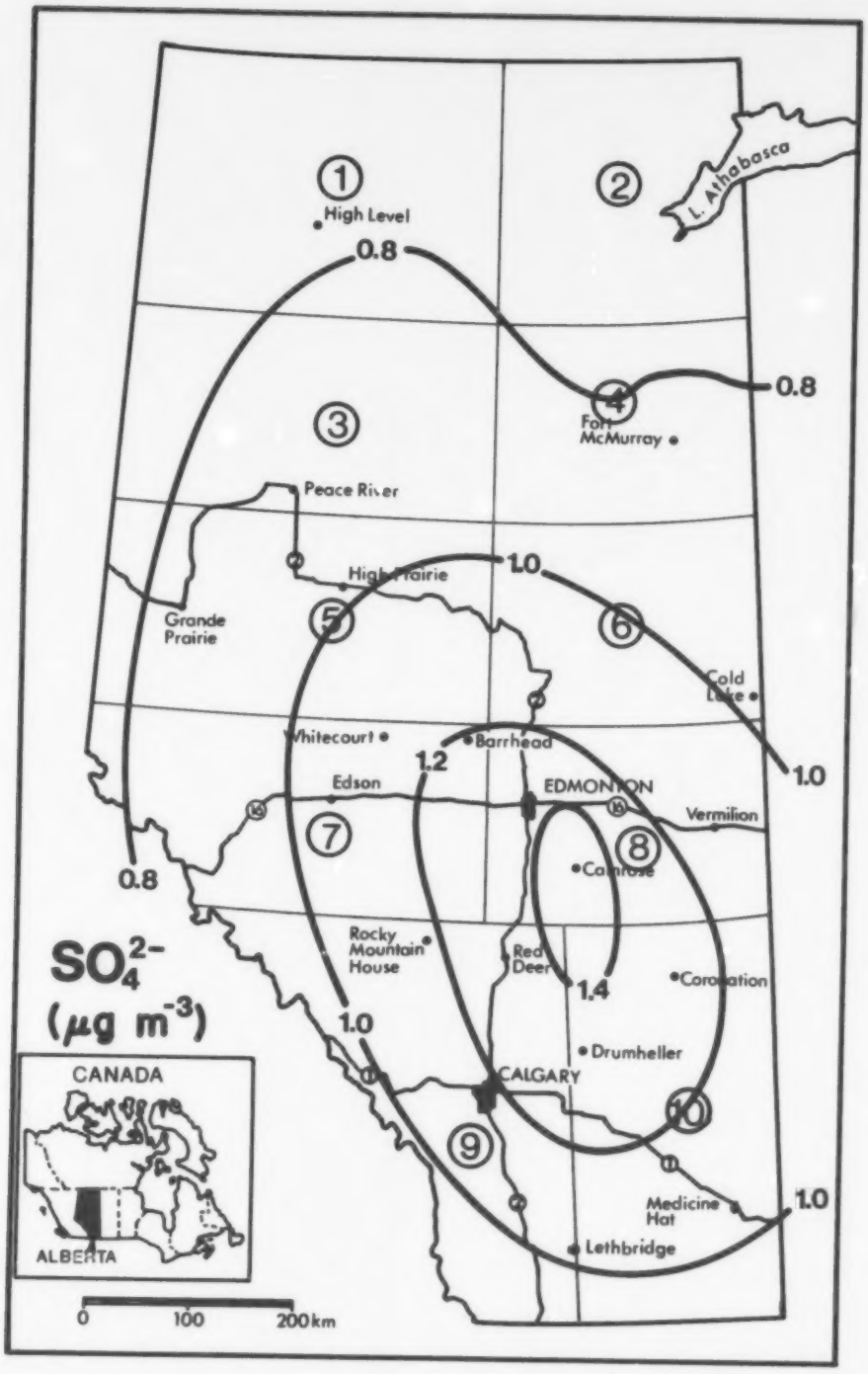


**Figure 26.** Average annual $SO_4^{2-}$ concentrations - future scenario ($\mu g\ m^{-3}$).

## 8. EFFECTS OF ACIDIC AND ACIDIFYING AIR POLLUTANTS ON SELECTED ENVIRONMENTAL COMPONENTS

In a real sense, all of the previous portions of this report have been a prologue to the main concern of ADRP: Are acidic or acidifying air pollutants causing environmental effects in Alberta? **Field work to observe possibly affected areas was not a part of the study to this point. Appropriate models can greatly narrow the geographic area to be searched during such field studies, as well as the media to be investigated.** A series of effects models, working from the previous models of pollutant dispersion and deposition, were constructed or adapted in an attempt to locate any geographic areas and environmental components likely to be affected by present or potential levels of pollutant emissions. The previous modelling gave reasonable estimates of seasonal and annual mean pollutant concentrations, but no information concerning the variability of individual short-term concentrations contributing to that average. If information is desired on the range of concentrations to be expected and the frequency of occurrence of concentrations within that range, then a different sort of model must be used in which more realistic, fluctuating meteorological conditions are introduced. After a study of possible models, a U.S. Environmental Protection Agency model called ISC (Industrial Source Complex) was adapted for the purposes in the scale of the present study, and was shown to give reasonably realistic results. It has been found that such models have very modest success in predicting accurately the concentration at a point on a given day and at a given hour. However, because of the statistical nature of atmospheric diffusion, they are far more successful in forecasting values such as the maximum hourly concentration during a season, or the number of times concentration will exceed a threshold value.

For verification, concentration fields were computed for three receptor sites in the general vicinity of **Crossfield**, Receptor 1 being similar in exposure to **Crossfield East**, and Receptors 2 and 3 more like **Crossfield West**. Table 22 displays the results of the modelling in comparison with the experimentally determined values at the two **Crossfield sites**. While the match is not perfect, and in particular the percentile values are higher in the models, **the match is within the normal margin of error of most modelling exercises**. The agreement on maximum values is particularly good for Receptor 1.

This is of importance, because one of the major questions framed in the planning of ADRP was the impact of acidic and acidifying pollutants on agricultural crops. Acidification as such is unlikely to produce significant effects on crops because of the practice of soil fertilization and liming, **so the most probable source of any significant effect on plants would be the direct toxicity of $SO_2$.** By contrast, nitrogen oxides by themselves are not considered deleterious to plants at any of the concentrations experienced in the Province.

**TABLE 22.** A comparison of model-generated and monitored $SO_2$ frequency distributions of one-hour concentrations (ppb).

| | Percentiles | | | Maximum |
|---|---|---|---|---|
| | 95 | 99 | 99.5 | |
| **Monitored Data** | | | | |
| **Crossfield West** | | | | |
| 1985-86 | 2.0 | 10.8 | 16.0 | 79 |
| 1986-87 | 1.7 | 8.6 | 11.9 | 84 |
| **Crossfield East** | | | | |
| 1985-86 | 2.0 | 17.1 | 24.3 | 70 |
| 1986-87 | 4.9 | 22.8 | 31.5 | 92 |
| **Model-Generated Data** | | | | |
| Receptor 1 | | | | |
| 1986 | 8.7 | 25.5 | 47.0 | 78 |
| 1987 | 8.3 | 27.2 | 41.0 | 79 |
| Receptor 2 | | | | |
| 1986 | 6.5 | 13.9 | 17.8 | 42 |
| 1987 | 5.9 | 12.0 | 14.6 | 34 |
| Receptor 3 | | | | |
| 1986 | 5.9 | 13.5 | 16.3 | 40 |
| 1987 | 5.4 | 12.1 | 16.8 | 46 |

Recent studies of the effects of gaseous pollutants on plants have revealed that annual or seasonal means of such pollutants are very poor measures of their effects on plant development. The reason can be explained by analogy: Normal human exposure to $H_2S$ is, in most environments, effectively zero. However, a concentration of some thousands of ppm would be lethal in a few seconds. Although the victim's annual average exposure would still be very near zero, he would still be dead. In the same way, the magnitude and duration of concentration peaks and frequency of exposure carry far more weight with regard to effects on plants than do long-term averages, unless these averages are extremely high.

As noted earlier, no studies of pollutant effects on trees were undertaken, or called for, in the program. The specific crops selected for study were alfalfa, which is widely recognized as being particularly sensitive to $SO_2$ effects, and wheat, which is generally considered rather tolerant of exposure. In fact, **the modelling showed no concentrations approaching the levels found to affect the development of wheat crops** and, therefore, the matter was not pursued further.

To predict alfalfa growth, proven model (ALSIM 1) was employed at three sites: **Crossfield, Barrhead, and Cold lake**. This model used meteorological data but made no

allowance for the impact of air pollutants. Computed yields were compared with actual reported yields. If reported yields were markedly less than those predicted by the model, it was then assumed that some environmental factor could be operative.

The model was used with: (a) monthly average climatological values for the actual year and month, (b) normal average climatological values for the month, (c) actual daily data reported at a nearby weather station, and (d) climatological average plus and minus one standard deviation. The results are displayed in Table 23.

Reports from **Crossfield** are for mixtures of alfalfa with other grasses. Therefore, they should be multiplied by 1.5 or 2.0 to compare against model simulated yields under "Actual 1986-87 Daily Data". Inspection of Table 23 thus shows that, **at both Crossfield and Cold Lake, the forecast yields**, particularly those employing the actual daily data, **were close to the true field values reported by growers in the area**. On the other hand, **the figures for Barrhead show yields to be roughly half of the model values**. Accordingly, attention was centered on possible effect of environmental sulphur dioxide on alfalfa yields in the **Barrhead area**, although some modelling was also done for **Crossfield**.

S.V. Krupa (Responses of Alfalfa to Sulfur Dioxide Exposures from the Emissions of the NSP-SHERCO Coal-Fired Power Plant Units 1 and 2, Vol. 1, Report submitted to Northern States Power Company, Minneapolis, Minnesota, 236 pp., 1987) observed the growth of alfalfa in a variety of well-monitored environments, and developed a multivariate regression model that accurately forecast the alfalfa leaf dry weight per 100 stems during the growing season of 1985 and 1986. Since the model is statistical, it can only reliably fit the data for the Minnesota area, the combinations of meteorological and other parameters encountered there, and the alfalfa varieties grown. It has not been validated for the counterparts of these situations in Alberta. However, since it is essentially the only model having any credibility for the low average concentrations encountered, it was applied with parameters appropriately taken from actual and modelled data. The results are displayed in Table 24.

The absolute magnitude of the growth and of the change in growth requires verification by counterpart experiments made locally in the Alberta environment. However, the model displays the known phenomena of growth enhancement as well as growth inhibition; in fact, **in the Crossfield locations, it appears that the low levels of $SO_2$ may well be more beneficial than detrimental**. At **Barrhead**, however, half of the calculations lead to growth inhibition, raising the possibility, although not proving it, that **$SO_2$ exposure is one of the environmental parameters, if not the only parameter, responsible for lower yields found there compared with theoretical expectations**. This is obviously an area calling for further investigation. Attention should also be directed to the nutritional quality of the crop, as this may be affected by low-level exposure to $SO_2$.

**TABLE 23.** Computer model simulated, and field reported, harvested yields (tons acre$^{-1}$) of alfalfa in Alberta, Canada, under various non-pollution weather regimes.

| Location | Weather Patterns Used for Alfalfa Crop Growth Simulations | | | | | |
|---|---|---|---|---|---|---|
| | Field Reported | Actual[1] 1986-87 Monthly Average | Long-Term Normal Monthly Average | Actual 1986-87 Daily Data | Long-Term Normal +1 Std. Dev. Mon. Avg. | Long-Term Normal -1 Std. Dev. Mon. Avg. |
| **Crossfield** | | | | | | |
| Yr 1 Cut 1[2] | 2.5 | 2.94 | 2.91 | 2.00 | 3.12 | 1.99 |
| Yr 2 Cut 1 | 0.5[4] | 2.39 | 2.63 | 1.29 | 3.30 | 0.97 |
| Yr 2 Cut 2 | 0.75-1.0[4] | 1.76 | 2.31 | 1.94 | 2.26 | 0.75 |
| Total | 1.25-1.5[4]<br>2.0[3] | 4.15 | 4.94 | 3.23 | 5.56 | 1.72 |
| **Barrhead** | | | | | | |
| Yr 1 Cut 1 | 0.6 | 1.84 | 1.92 | 1.86 | 1.83 | 0.55 |
| Yr 1 Cut 2 | 1.1[5] | 2.30 | 2.44 | 2.20 | 2.39 | 2.02 |
| Total | 1.7[5]<br>2.0-2.6[6] | 4.14 | 4.36 | 4.06 | 4.22 | 2.57 |
| Yr 2 Cut 1 | 1.1[5] | 2.45 | 2.62 | 2.37 | 3.20 | 0.05 |
| Yr 2 Cut 2 | 0.9[5] | 2.00 | 2.02 | 1.75 | 2.32 | 0.00 |
| Total | 2.0[5]<br>2.0-2.6[6] | 4.45 | 4.64 | 4.12 | 5.52 | 0.05 |
| **Cold Lake** | | | | | | |
| Yr 1 Cut 1 | | 1.95 | 2.25 | 1.77 | 2.18 | 1.32 |
| Yr 1 Cut 2 | 1.76[7] | 2.11 | 2.12 | 1.80 | 2.26 | 1.52 |
| Total | 2.0-2.4[8] | 4.06 | 4.37 | 3.57 | 4.44 | 2.84 |
| Yr 2 Cut 1 | 1.5-1.9[9] | 2.75 | 2.39 | 0.96 | 3.13 | 0.88 |
| Yr 2 Cut 2 | 1.4-1.7[10]<br>1.0[7] | 1.66 | 1.89 | 1.57 | 1.96 | 2.18 |
| Total | 3.2-3.3[11] | 4.41 | 4.28 | 2.53 | 5.09 | 3.06 |

[1] Refers to solar radiation, air temperature, and precipitation data used.

[2] Only one cutting reported for 1986 in the Crossfield area.

[3] Larry Welsh, personal communication; for mixtures, not pure stands.

[4] Local crop specialist, personal communication; for mixtures, not pure.

[5] Fred Boise, personal communication.

[6] Alfalfa production plant operator for Legal and Barrhead areas, personal communication.

[7] Local grower producing very high crude protein, pure stand alfalfa for sale from second cutting; first cutting used as silage and not recorded; personal identity kept anonymous.

[8] Angus variety: 2.0; Beaver variety: 2.3; Rambler (creeping root) variety: 2.4; (Bjorn Berg, personal communication); pure stands.

[9] Algonquin (tap root) variety: 1.5; Rambler variety: 1.9; (Bjorn Berg, personal communication); pure stands.

[10] Rambler variety: 1.4; Algonquin variety: 1.7; (Bjorn Berg, personal communication); pure stands.

[11] Algonquin variety: 3.2; Rambler variety: 3.3; (Bjorn Berg, personal communication; pure stands.

**TABLE 24.** Comparison of alfalfa leaf dry weight per 100 stems without and with modelled ambient sulphur dioxide pollution using the Krupa multivariate exposure-response model (Krupa 1987, refer to page 59).

| | | | | Alfalfa Leaf dry wt g $100\ stems^{-1}$ | | |
|---|---|---|---|---|---|---|
| Area | Location | Year | Harvest | Without | With $SO_2$ | Change |
| Crossfield | 1 | 1987 | 2 | 40.0 | 71.0 | + |
| Crossfield | 2 | 1987 | 1 | 23.0 | 60.0 | + |
| Crossfield | 2 | 1987 | 2 | 40.0 | 78.0 | + |
| Crossfield | 3 | 1987 | 1 | 23.0 | 18.0 | - |
| Crossfield | 3 | 1987 | 2 | 40.0 | 48.0 | + |
| Barrhead | 1 | 1986 | 1 | 24.0 | 38.0 | + |
| Barrhead | 1 | 1986 | 2 | 16.0 | 19.0 | + |
| Barrhead | 1 | 1987 | 1 | 35.0 | 44.0 | + |
| Barrhead | 1 | 1987 | 2 | 38.0 | 35.0 | - |
| Barrhead | 2 | 1986 | 1 | 24.0 | 10.0 | - |
| Barrhead | 2 | 1987 | 1 | 35.0 | 34.0 | - |
| Barrhead | 2 | 1987 | 2 | 38.0 | 36.0 | - |
| Barrhead | 3 | 1986 | 1 | 24.0 | 128.0 | + |
| Barrhead | 3 | 1987 | 1 | 35.0 | 33.0 | - |
| Barrhead | 3 | 1987 | 2 | 38.0 | 104.0 | + |

In summary, modelling of the impact of $SO_2$ on alfalfa gave mixed results. Nevertheless:

- **Alfalfa yields in the Barrhead area (Region 7) are lower than expected.**
- **Peak $SO_2$ exposures (10 minute) at Crossfield are more than 30% higher than the continuously measured values used by Krupa.** This is not accounted for in the present model which uses 1-hour exposures. In the absence of monitoring, there is no information on peak exposures at **Barrhead** (Region 7).
- In the construction of his model, Krupa monitored and modelled only the impact of $SO_2$, so the effect of **exposure to other pollutants is unknown.** Significant elevated ozone levels are known to occur in the **Crossfield area**, and it is further known that, under appropriate conditions, exposure to $O_3$ and $SO_2$ can have an additive or more-than-additive effect.

It is therefore recommended that **appropriate research be undertaken to construct and validate models of alfalfa growth** under the specific soils, climatological, and pollutant exposure conditions of Alberta. Until this is done, questions will remain concerning the present and future impact of pollutants on agricultural crops in the Province.

One of the major concerns in the study of acidic and acidifying deposition has been the impact of the deposited materials on soils. Many agricultural crops such as alfalfa are very sensitive, being harmed by even slight soil acidity. **On managed soils, the impact of the usual soil treatments is enormously greater than any effect of acidic or acidifying deposition.** Consequently, the effects of acidic deposition on soil manifests itself, so far as any direct economic impact is concerned, in range land and forested areas. Forest soils are almost invariably acidic, predominantly because of the biological recycling of litter, a process that produces organic and inorganic acids.

As previously noted, field measurements of environmental factors other than air chemistry were not a part of the research prior to **Critical Point I**. It was intended that the research carried out in the first phase of this study would pinpoint areas of concern, thus narrowing the field for subsequent research, should possible impacts be detected.

Fortunately, a series of soil surveys have characterized a large number of Alberta soils. A recently developed model of soil acidification was identified that makes use of the same soil parameters that are tabulated in these surveys, and this was applied. The deposition data are those previously tabulated in Table 18 and identified in that table as "mean" and "maximum" deposition values, the maximum annual deposition values corresponding to the present individual 90th percentile figures. While there is some difference among the various deposited materials, these 90th percentile figures correspond to a mean deposition roughly three times as great as the present mean value.

The soils selected for modelling constitute a cross-section of soils generally characterized as sensitive or moderately sensitive. Modelling was carried out with the assumption that the deposition figures are characteristic of an entire region as defined here, and the soils were subjected to the calculated deposition for the region in which they occur. The five regions with the largest sources of acidifying pollutants were considered; i.e., Regions 3, 4, 6, 7, and 9. In addition, a separate calculation was made for the mountainous area common to Regions 7 and 9, using deposition data computed from the monitoring station at **Fortress Mountain**.

**It must be noted that**, at virtually every step, this chain of **modelling is extremely conservative**, in the sense that it overestimates the impact of the pollutants. In most cases, therefore, a change in soil chemistry predicted by the model to take, say, 30 years will probably take at least twice as long.

The model presented the data in a number of ways. One of the most easily understood is given in Table 25 in the form of time to reach a series of threshold values of pH. In each case, the calculation was done for the present mean acid loading and the maximum loading, as these were explained previously.

**TABLE 25.** Model predictions of time (years) required for soils to reach threshold pH levels at estimated current and future loadings of acidic deposition.

| Soil Type | Acid Loading $kmol(H^+)ha^{-1}y^{-1}$ | Initial pH | Threshold pH | | |
|---|---|---|---|---|---|
| | | | 5.0 | 4.0 | 3.6 |
| | | Region 3 | | | |
| Heart | 0.19 | 5.3 | 145 | >300 | >300 |
| | 0.3 | 5.3 | 65 | >300 | >300 |
| Demmitt | 0.19 | 5.3 | 280 | >300 | >300 |
| | 0.39 | 5.3 | 130 | >300 | >300 |
| Alcan | 0.19 | 4.4 | — | >300 | >300 |
| | 0.39 | 4.4 | — | 175 | >300 |
| Boundary | 0.19 | 4.1 | — | 230 | >300 |
| | 0.39 | 4.1 | — | 100 | >300 |
| | | Region 4 | | | |
| Firebag | 0.22 | 4.2 | — | 15 | 160 |
| | 0.86 | 4.2 | — | 5 | 20 |
| Mildred | 0.22 | 4.8 | — | 280 | >300 |
| | 0.86 | 4.8 | — | 50 | 90 |
| Kinosis | 0.22 | 4.0 | — | 0 | >300 |
| | 0.86 | 4.0 | — | 0 | 80 |
| Legend | 0.22 | 4.1 | — | 110 | >300 |
| | 0.86 | 4.1 | — | 20 | 160 |
| | | Region 6 | | | |
| Nestow | 0.18 | 4.2 | — | 15 | 70 |
| | 0.33 | 4.2 | — | 10 | 35 |
| Nicot | 0.18 | 5.8 | >300 | >300 | >300 |
| | 0.33 | 5.8 | 195 | >300 | >300 |
| Codesa | 0.18 | 5.9 | >300 | >300 | >300 |
| | 0.33 | 5.9 | >300 | >300 | >300 |
| Falun | 0.18 | 5.8 | >300 | >300 | >300 |
| | 0.33 | 5.8 | >300 | >300 | >300 |
| Tawatinaw | 0.18 | 5.9 | >300 | >300 | >300 |
| | 0.33 | 5.9 | >300 | >300 | >300 |
| La Corey | 0.18 | 5.4 | 295 | >300 | >300 |
| | 0.33 | 5.4 | 155 | >300 | >300 |

continued . . .

**TABLE 25. (concluded)**

| Soil Type | Acid Loading $kmol(H^+)ha^{-1}y^{-1}$ | Initial pH | Threshold pH | | |
|---|---|---|---|---|---|
| | | | 5.0 | 4.0 | 3.6 |
| | | Region 7 | | | |
| Culp | 0.28 | 5.8 | >300 | >300 | >300 |
| | 0.47 | 5.8 | 60 | >300 | >300 |
| Cooking Lake | 0.28 | 6.2 | >300 | >300 | >300 |
| | 0.47 | 6.2 | >300 | >300 | >300 |
| Hubalta | 0.28 | 5.6 | >300 | >300 | >300 |
| | 0.47 | 5.6 | >300 | >300 | >300 |
| Berland | 0.28 | 5.7 | >300 | >300 | >300 |
| | 0.47 | 5.7 | 210 | >300 | >300 |
| Red Willow | 0.28 | 5.6 | >300 | >300 | >300 |
| | 0.47 | 5.6 | 200 | >300 | >300 |
| Ponoka | 0.28 | 5.7 | >300 | >300 | >300 |
| | 0.47 | 5.7 | >300 | >300 | >300 |
| Nosehill | 0.28 | 4.4 | — | 280 | >300 |
| | 0.47 | 4.4 | — | 155 | >300 |
| | | Region 9 | | | |
| Spruce Ridge | 0.48 | 4.4 | — | 220 | >300 |
| | 1.14 | 4.4 | — | 95 | 215 |
| Elbow | 0.48 | 5.0 | 0 | >300 | >300 |
| | 1.14 | 5.0 | 0 | >300 | >300 |
| Antler | 0.48 | 5.8 | >300 | >300 | >300 |
| | 1.14 | 5.8 | 270 | >300 | >300 |
| Delacour | 0.48 | 5.7 | 295 | >300 | >300 |
| | 1.14 | 5.7 | 105 | 275 | >300 |
| Dunvargan | 0.48 | 5.9 | >300 | >300 | >300 |
| | 1.14 | 5.9 | 255 | >300 | >300 |
| | | Mountain Region | | | |
| Egypt | 0.24 | 4.0 | — | 0 | >300 |
| | 0.67 | 4.0 | — | 0 | 110 |
| Topaz | 0.24 | 4.6 | — | 125 | 150[1] |
| | 0.67 | 4.6 | — | 35 | 140 |

[1] Minimum pH reached in this soil was 3.9

The threshold pH of 5 was selected as one unit above the level at which there are essentially no impacts of soil acidity. At pH 4, the buffering of the soil has shifted from cation exchange to the equilibria involving aluminum. When a pH of 3.6 is reached, aluminum concentrations are high enough that aluminum toxicity may become a serious limiting factor to plant growth generally. It will be noted that a few of the selected soils already have reached a pH of 4. Where these soils are coarse and sandy, virtually the only remaining buffering capacity is in the organic litter layer, which is not considered in the present model.

Examination of the table leads to the conclusion that **the soils of Region 3 are uniformly quite resistant to acidification**, whether deposition is assumed to continue at the present rate, or allowed to increase by more than a factor of 2. In contrast, **the soils of Region 4 appear more sensitive**, although a continuation of present deposition rates would require, in all cases, well over a century before the lowest threshold was passed. **In Region 6, the Nestow soil is susceptible to acidification** with both deposition scenarios, **but the balance of the soils considered were highly resistant, as were the soils of Regions 7 and 9. In the mountains, the Topaz soil**, although less acidic today, **appears to have less resistance to acidification than the Egypt soil**.

An important impact of reduced soil pH is a shift in the balance between available nutrient trace elements and available toxic trace elements. Another is the decreased activity of the microorganisms responsible for litter decomposition and nutrient recycling. Acidification occurs naturally in forests, as previously noted, but it can be accelerated by anthropogenic inputs of acidifying substances, and greatly retarded by the application of soil management practices.

**The research prior to Critical Point I has thus identified specific soils (and thus specific locales) in which accelerated acidification may have been occurring**, or will occur with increased pollutant inputs. **Coordinated field and laboratory research will be needed** to determine more accurately the true deposition rate of acidic and acidifying substances, to test the validity of the models employed in the present study, and to extend the models to include the effects of factors not presently included, such as the impact of the organic fraction of these soils. Further studies are also needed on the response of plants, especially trees and their symbionts, to varying degrees of soil acidification.

**A final area of concern is the possible acidification of surface waters** within the Province. Available data were compiled on the present chemistry of nearly 500 lakes and 19 rivers predominantly in the five regions having the highest emissions of sulphur compounds, Regions 3, 4, 6, 7, and 9. In addition, the mountainous portions of Regions 7 and 9 were considered separately and identified as Regions 7b and 9b, respectively.

The current data base, while it represents an impressive number of waterways, affords little direct information on possible changes in water chemistry. A modelling approach was again used. As before, the model chosen was extremely conservative. It was assumed that all deposited sulphur arrived as $H_2SO_4$, and that it was transmitted without loss, as such, to the lakes in the watershed, essentially by the water volume represented by the difference between precipitation and evapotranspiration. Upon arrival at the lake or stream, it was assumed to titrate the available bicarbonate alkalinity without interaction with other substances. In addition, the deposition rates previously derived were assumed to be characteristic of the entire region, ignoring the fact that, in Regions 7 and 9 at least, the mountainous portions had far lower deposition rates than did the plains. To correct this, separate computations were made for the two mountainous areas. A final calculation was made on the assumption that, for each area, new local sources added were sufficient to raise deposition to the values experienced at **Crossfield East**—an ultimate "worst case" scenario, and markedly more extreme than the one utilized in studies of effects on plants and soils.

Table 26 shows the distribution throughout each region of lake water chemistry, together with a computed "original alkalinity" predicated on the assumption that sulphate has already neutralized an equivalent amount of alkalinity. Note that this is the present sulphate content of the lake water, not the deposition. Table 27 displays the impact of deposition on these waters, first utilizing the present levels of deposition, and then the worst case, in which deposition rises to the level measured at **Crossfield East**. The final results are shown in Table 28. **This extremely conservative calculation points to Regions 7 and 9 as the areas of concern**. However, it must be remembered that a number of the lakes in these regions are located in the mountains, and that this calculation assumes that deposition rates there are similar to those in the more heavily affected foothills and plains of those regions. **Correction to deposition rates characteristic of the mountain areas greatly decreases the percentage of lakes threatened by acidification. In all regions, the introduction of major new sources greatly increases the risk of lake acidification.**

By contrast, **the rivers appear quite immune to acidification** (Table 29). It appears that river acidification is not a serious problem in Alberta, and no further modelling was explored in these cases.

That **the present lake model is almost certainly overestimating the impact of acidifying deposition** is shown graphically by Figure 27, which plots, for all lakes, the present sulphate content as a function of the sum of calcium, magnesium, sodium, and potassium. Their relationship is essentially linear, and the correlation coefficient is 0.76, which is highly significant. In contrast, there is essentially no relationship between lake pH and sulphate content, or between lake sulphate and calculated deposited sulphate. It is probable that sulphate content is determined much more by sources of sulphur in the aquifers that feed the lakes;

**TABLE 26.** Regional and sub-regional estimated original (pre-acidification) alkalinity, current alkalinity, current lake sulphate concentrations, and current pH values (all values in mg $L^{-1}$ except pH).

| Emission Region | pH | $SO_4^{2-}$ | Alkalinity Current | Alkalinity Original |
|---|---|---|---|---|
| Sub-region 7b | | | | |
| mean | 7.93 | 19.40 | 83.8 | 103.9 |
| median | 8.10 | 8.50 | 74.0 | 82.8 |
| min. | 6.10 | 0.20 | 0.2 | 0.4 |
| max. | 8.80 | 294.00 | 309.0 | 614.8 |
| Sub-region 9b | | | | |
| mean | 7.90 | 19.60 | 119.2 | 139.6 |
| median | 7.90 | 5.10 | 55.0 | 60.3 |
| min. | 6.80 | 0.30 | 6.8 | 6.8 |
| max. | 10.20 | 1282.00 | 5451.0 | 6794.3 |
| Region 3 | | | | |
| mean | 7.47 | 53.56 | 104.3 | 160.0 |
| median | 7.50 | 61.25 | 105.0 | 168.7 |
| min. | 6.40 | 2.51 | 15.0 | 17.6 |
| max. | 8.10 | 180.00 | 179.0 | 355.8 |
| Region 4 | | | | |
| mean | 7.37 | 5.10 | 59.2 | 64.5 |
| median | 7.30 | 2.98 | 51.5 | 54.6 |
| min. | 5.90 | 2.5 * | 6.0 | 8.6 |
| max. | 9.20 | 20.0 | 140.0 | 158.7 |
| Region 6 | | | | |
| mean | 8.10 | 9.61 | 128.0 | 138.0 |
| median | 8.20 | 15.39 | 135.0 | 151.0 |
| min. | 7.50 | 2.5 * | 50.0 | 52.6 |
| max. | 8.80 | 29.04 | 200.0 | 230.2 |
| Region 7 | | | | |
| mean | 7.97 | 30.96 | 86.4 | 118.6 |
| median | 8.10 | 15.29 | 80.8 | 96.7 |
| min. | 6.10 | 0.20 | 0.2 | 0.4 |
| max. | 9.26 | 426.98 | 724.1 | 309.0 |
| Region 9 | | | | |
| mean | 7.96 | 72.98 | 184.8 | 260.7 |
| median | 7.90 | 5.58 | 65.5 | 71.3 |
| min. | 6.80 | 0.96 | 6.8 | 7.5 |
| max. | 10.20 | 2130.9 | 6300.0 | 8188.6 |

Original Alkalinity = Alkalinity + 1.04 $[SO_4^{2-}]$

* Value of $SO_4^{2-}$ Based on 1/2 Analytical Detection Limit

Sub-regions 7b and 9b represent the mountainous portions of the major Emission Regions 7 and 9, respectively.

**TABLE 27.** Estimated loss of alkalinity of surface waters (mg $L^{-1}$ of $CaCO_3$) due to atmospheric sulphur deposition using various assumptions. (The acid/base chemistry of deposition is 100% effective in reducing alkalinity; no watershed modification of precipitation chemistry by soils, biology, geology, or aquatic sediments).

| Location | Precipitation pH | (1) Total S ($H_2SO_4$) | (2) Wet Only ($H_2SO_4$) | (3) Dry Only ($H_2SO_4$) | (4) $HCO_3^-$ Wet Deposition | (5) Potential Alkalinity Loss at Present | (6) Potential Additional Alkalinity Loss With Crossfield Deposition | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | Additive Loss | Total Loss |
| Region 3 | 5.11 | 14.2 | 5.4 | 8.8 | 0.5 | 8.3 | 30.8 | 39.1 |
| Region 4 | 6.01 | 9.9 | 4.6 | 5.3 | 0.8 | 4.5 | 4.9 | 9.4 |
| Region 6 | 5.21 | 19.6 | 4.9 | 14.7 | 0.1 | 14.6 | 40.2 | 54.8 |
| Region 7 | 6.02 | 14.0 | 6.4 | 7.6 | 0.9 | 6.7 | 5.5 | 12.2 |
| (Jasper 7b) | 5.07 | 3.8 | 2.5 | 1.3 | — | 1.3 | 6.6 | 7.9 |
| Region 9 | 5.08 | 27.7 | 11.9 | 15.7 | 0.2 | 15.5 | 6.3 | 21.8 |
| (Banff, 9b) | 5.07 | 3.8 | 2.5 | 1.3 | — | 1.3 | 5.8 | 7.1 |
| (Crossfield East) | 5.10 | 70.7 | 27.0 | 43.9 | 17.0 | 26.9 | 0 | 26.9 |

* Precipitation pH = mean annual volume weighted pH.

1 = $H_2SO_4$ as converted alkalinity (1.04 x $SO_4^{2-}$).
1 = Column 2 + Column 3.
5 = Column 3 + Column 4.

**TABLE 28.** Percent of lakes examined by region which have the potential for all mean annual alkalinity to be lost by superimposition of deposition equivalent to **Crossfield East** (A), or under present deposition levels (B).

| Region | Percent of Lakes Examined With the Potential to Lose All Alkalinity | |
|---|---|---|
| | A | B |
| 3 | 12.5 | 0.0 |
| 4 | 13.6 | 0.0 |
| 6 | 5.3 | 0.0 |
| 7 (whole region) | 20.9 | 7.2 |
| 7b (mountains only)* | 9.5 | 1.6 |
| 9 (whole region) | 5.7 | 2.9 |
| 9b (mountains only)* | 3.8 | 1.0 |

Assumptions used are worst case—all sulphur deposition is $H_2SO_4$; point source does not introduce bases into atmosphere and increased atmospheric acidity does not increase reactions of acids with bases. All deposited $H_2SO_4$ is assumedi to be perfectly (100%) transmitted to receptor waters.

* Sub-regions 7b and 9b represent the mountainous portions of the whole Regions 7 and 9, respectively, and were derived on the basis of deposition values for **Fortress Mountain** and evapotranspiration values for **Jasper**.

**TABLE 29.** Relationship between mean annual pH, $SO_4^{2-}$, alkalinity, original alkalinity, and potential atmospheric deposition of acid forming sulphates (converted to alkalinity equivalents). For all regional rivers. (All values in mg $L^{-1}$ except pH in units).

| Emission Regions | pH | $SO_4^{2-}$ | Present Alkalinity ($CaCO_3$) | Original Alkalinity | Present Potential Alkalinity Loss* | Future Possible Alkalinity Loss** | Assessment of Sensitivity |
|---|---|---|---|---|---|---|---|
| 3 | 8.01 | 37.57 | 130.8 | 169.87 | 8.3 | 39.1 | Not Sensitive |
| 4 | 7.50 | 11.42 | 210.6 | 222.48 | 4.5 | 9.4 | Not Sensitive |
| 6 | 7.83 | 2.46 | 209.6 | 212.16 | 14.6 | 40.2 | Not Sensitive |
| 7 | 7.53 | 7.00 | 119.4 | 126.68 | 6.7 | 5.5 | Not Sensitive |
| 9 | 8.17 | 214.30 | 302.8 | 525.67 | 15.5 | 21.8 | Not Sensitive |

* Present potential based on estimated wet + dry $SO_4^{2-}$ deposition (converted to alkalinity equivalents) — net wet $HCO_3^-$.

** Future potential based on the imposition of **Crossfield East** scenario on each region.

All sulphate loadings converted to alkalinity equivalents; ($SO_4^{2-}$ x 1.04) = alkalinity.

many of these aquifers are known to pass through coal beds or other sources of terrestrial sulphur.

Thus it appears that **few, if any, water bodies in the Province are being significantly affected by present levels of sulphur deposition**; it also appears that a potential for future acidification does exist, **should the Province at a later date become intensively industrialized.**

By its nature, the model used is incapable of considering short-term events. Therefore, it cannot preclude the possibility of short-term acidification of waterways, for example, during spring runoff. During this period, there is marked dilution of all water bodies, reducing the buffering capacity, and simultaneously the introduction of acidic accumulation from the snowpack derived from both natural and manmade sources during the winter. Since this period is also the spawning season when fish are most sensitive to an acidic environment, the **possibility exists of an adverse effect**, even in water bodies that, under average circumstances, may not be acidified.

**Research aimed specifically at examining the potential for short-term changes in water chemistry, as well as longer-term studies of the response of some of the more sensitive lakes to present input levels of acidic and acidifying pollutants is obviously warranted. A far more detailed data base is required for at least some water bodies**, including both water chemistry and aquatic biota, and **the studies need to have sufficient duration to permit identification of any trends in acidity**, as well as response to seasonal effects. Once again, the preliminary modelling undertaken here has identified candidate areas. Since a key question not addressed in present models is the modification of wet deposition by soil on its way to the receiving lake or river, **these studies should be suitably integrated with**

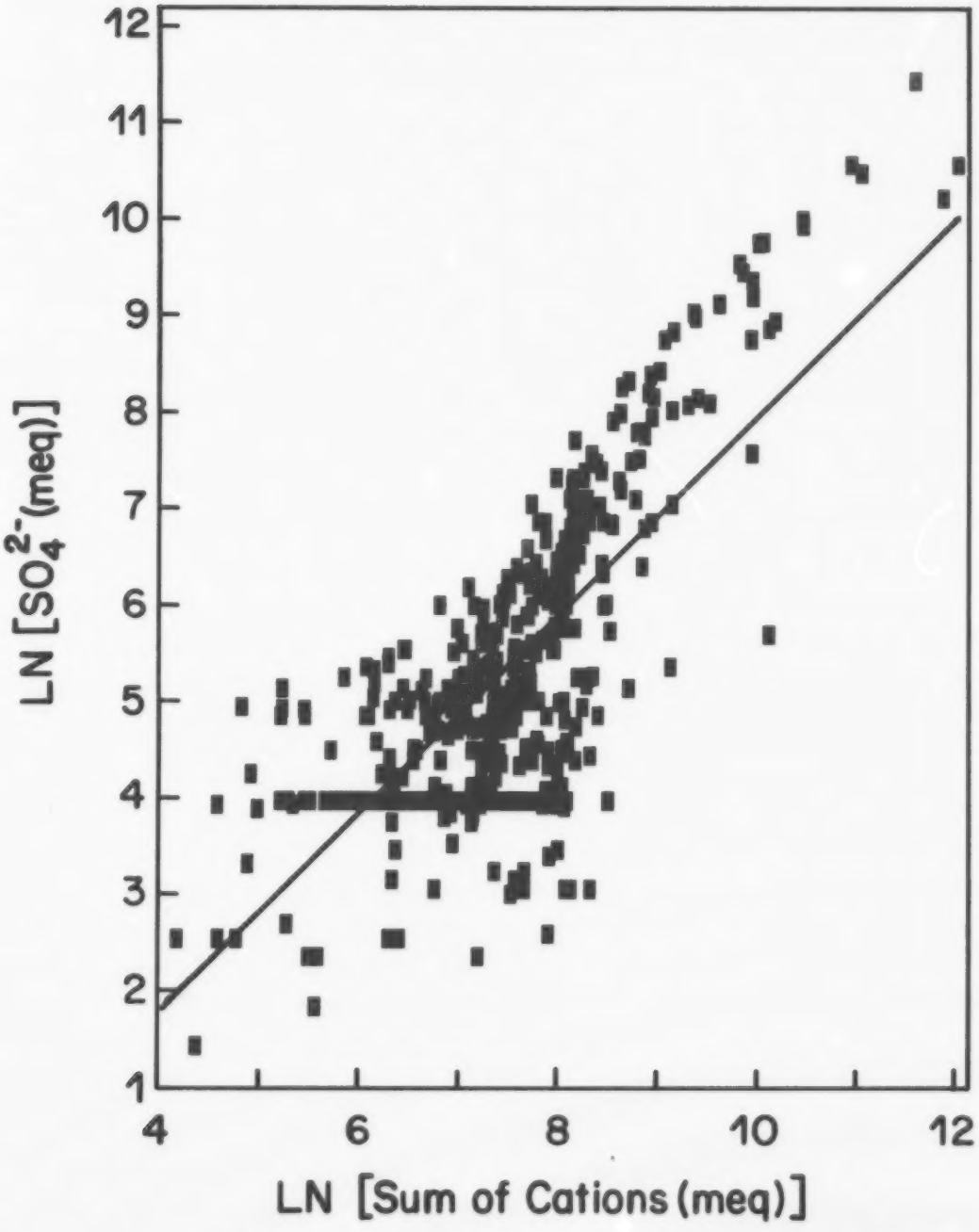


**Figure 27.** Relationship between the natural logarithm of sulphate concentration and the natural logarithm of total cation concentration for 484 lakes.

studies of the response of soils to acidic deposition. This probably implies the study of lakes in forested watersheds.

It must be remembered that the model implied here is a risk model that considers, at each step, the worst alternative. There is little firm indication that, at present, any water bodies in the Province have been significantly impacted by acidic deposition.

## 9. CONCLUSIONS

Concern over present and future regional impacts of acidic or acidifying pollutants discharged within Alberta led to the initiation of the Acid Deposition Research Program, a unique product of cooperative support from the provincial Government and industry. It was designed to evaluate present and future risks of environmental impacts from the emission of nitrogen and sulphur pollutants within the Province.

The design called for two phases, identified by their endpoints in time, Critical Point I. and Critical Point II. It was intended with the first phase that a decision would be reached at Critical Point I. as to whether there was a need for a second phase. Research during the first phase, to Critical Point I., had three major components. The first of these was the preparation, by experts in the respective fields, of world literature reviews of all aspects of the problem of acidic deposition and its impacts. These reviews have been prepared and disseminated and should be an invaluable resource.

A second portion of the work was the installation and operation of three comprehensive field stations for measurement of chemical and meteorological parameters of the atmosphere. One was located in the pristine area close to Fortress Mountain, and obtained excellent data on the quality of air entering the Province, specifically from the west. The other two bracketed a point source near Crossfield. In general, ambient air at Crossfield West was basically modified by agricultural practice and human activity. Crossfield East received, in addition, the impact of the City of Calgary, of a major automotive traffic corridor, and of the point source. An exhaustive inventory was made of all significant sources of air pollutants in the Province. This inventory, coupled with source characterization studies, permitted allocation of ambient pollutants among the potential sources.

The third component was the application of the resulting knowledge of air chemistry to the evaluation of possible impacts of air pollutants on agricultural crops, soils, and surface waters. Field work on effects was not part of the mandate of the program to Critical Point I., nor was the consideration of possible impacts on forest ecosystems as such. Since this was essentially a risk assessment study, the models utilized were selected to be extremely conservative in the sense that they were far more likely to predict an effect

**where there was none than to fail to predict an effect that was actually occurring.** In each case, two scenarios were employed, one in which the present levels of deposition (and presumably, therefore, present emission levels) were continued indefinitely, and the other a type of "worst case" scenario. For crops and soils, this represented an increase from present mean levels to a mean equivalent to the present 90th percentile figure of individual measurements. In the case of surface waters, this was an increase, provincewide, to the ambient levels a few kilometres from the point source at Crossfield.

Disposition of the **literature reviews** has already been discussed. **They constitute a major resource of information,** and have already served well in the section of models for the evaluation of effects. They will also be valuable as continuing guides for future research, both in clearly indicating those areas in which there are serious gaps in our knowledge, and in preventing unnecessary duplication of studies.

**The air quality monitoring program generated a data base unmatched elsewhere in the world. Monitoring at the Fortress Mountain station has provided information on background air quality** at high altitudes, and has also **revealed the occasional incursion of high ozone concentrations** that most probably result from long-range transport of the pollutant from the urban centres that bracket the U.S.-Canadian border. **Monitoring at Crossfield showed,** as previously noted, **the modification of this background air by passage over the Province,** and both permitted the assignment of pollutants to probable source, and provided a large body of data for validation of pollutant dispersion models that were necessary to estimate pollutant concentrations elsewhere in the Province. Finally, **the combined data,** because of their sheer numbers and accuracy, **permitted a critical test of statistical techniques used** in the treatment of air monitoring data worldwide. **All data were best fit by the Weibull distribution,** which permitted back-calculation to supply reasonable values for data that were "missing" by virtue of being below the detection limits of the respective monitors. Meanwhile, **the accurate emission inventory greatly improved the credibility of the various models** of atmospheric transport that were the necessary first step in evaluation of effects.

Having this body of hard data, the next and final phase was the evaluation of pollutant impacts. To do this, it was necessary **to model both the short-term and the long-term dispersion of emitted pollutants** over the total area of the Province. The fit was well within the usual parameters of model performance. Lacking data at other sites, the researchers did not modify the models to improve their capabilities. Next, since pollutants generally exert their effects only when deposited on surfaces, typical deposition rates were computed using accepted techniques. As a final step, **models were selected,** in the most conservative fashion possible, **predicting the impact of these deposition rates on crops, soils, and surface waters.**

Given the conservatism of the models, it is extremely unlikely that, except in the immediate vicinity of point sources, there is any impact on any of these environmental components. Even extreme future increases in deposition would result in airborne concentrations too low to affect wheat. However, one area was discovered in eastern Region 7 in which alfalfa yields were well below those predicted by a model that does not take air pollutant impacts into account, and it is possible that sulphur dioxide could be one factor in the depression of these yields. The possibility is increased if this area also experiences the elevated ozone concentrations measured at Crossfield as a result of long-range transport. In a number of situations, the model employed also predicted a significant stimulation of the growth of alfalfa, rather than a reduction.

In this area, and elsewhere in the Province, the atmospheric deposition of acidifying substances to soils was quite without impact on managed soils, being totally overwhelmed by the effect of applied fertilizer and lime. However, the Province includes a number of soil types that are very slightly buffered and susceptible to acidification. Since these are virtually all forest soils they are already strongly acid, and, if they actually experience deposition of the magnitude of present computed levels, their further acidification could be significantly accelerated. Major increases in deposition could threaten other areas as well, assuming that the model employed is valid for these soils.

Lakes and rivers in Alberta are predominantly slightly alkaline and well buffered. Nevertheless, exceptions exist. These susceptible lakes are not evenly distributed throughout the Province and are primarily lakes surrounded by heavy forests and, hence, by soils that are already strongly acidic. No adequate time series of changing acidity in Alberta lakes exist to permit validation of models; thus the models utilized were grossly oversimplified.

With few exceptions, the models demonstrated no impacts on crops, soils, and surface waters. Small impacts on alfalfa growth were found in a few areas. Large increases in mean deposition levels, however, could impact alfalfa and similarly susceptible vegetation, particularly in areas that also experience high concentrations of ozone. Such increases could acidify soils and surface waters in a few susceptible areas.

## 10. RECOMMENDATIONS

Effects cannot be evaluated without knowing the magnitude of the causal factors, and modelling is no substitute for in situ measurement. Systematic measurement is a necessary precondition to the improvement of models, which can permit interpolation between widely spaced monitoring sites.

Experience during the program (to **Critical Point I.**) showed that **a number of atmospheric monitoring instruments recorded little of consequence. Future monitoring stations should continuously record $O_3$ and $SO_2$, but the bulk of the other pollutants of concern can be better determined using integrated samplers with vastly lower detection limits, such as the annular denuder.** It would also be of great value to **maintain a background measurement station**, both in terms of the fundamental knowledge gain, and for further study of the long-range transport of $O_3$ into the Province. **Simultaneous recording of meteorological parameters is essential to experimentally determine the rates of dry deposition of atmospheric pollutants. Studies of precipitation chemistry are required to determine wet deposition in selected areas.**

In view of the possibility of an environmental effect on alfalfa yields in the eastern portion of Region 7, **studies should be carried out in that region to ascertain the possible impact of combined sulphur dioxide and ozone on alfalfa yields.** Information from these studies would improve the statistical model, making it more applicable to the Alberta environment and Alberta varieties of alfalfa. In addition, **exposure studies of both forest and the crop plants must be undertaken to improve the prediction of response to ozone, sulphur dioxide, and nitrogen oxides.**

Since Alberta has a number of areas with acid-sensitive soils, **coordinated atmospheric and soil monitoring, further soil characterization studies, and studies of the impact on the organic portion of these soils** need to be made in selected areas. Further studies are needed of **nutrient cycling** in both susceptible and nonsusceptible soils. **The role of microorganisms responsible for the mineralization of both litter and other soil** inputs should be integrated with these studies, and the **ability of soils to immobilize sulphate** needs to be characterized as a function of soil type. The end result of these studies should be **greatly improved models for predicting the impact of acidic inputs on soils**, particularly in forest environments.

Surface water acidification generally involves the transport of deposited acidifying substances through soils, and their modification during this process. **Candidate sites for intensive studies of surface water chemistry should be selected as areas in which soil studies will also be conducted.** The ultimate goal is **the development of integrated models** that include the effects of surrounding soils on surface water acidification. In addition, **studies should be made of the effects of acidic episodes**, such as spring runoff, on the chemistry and biota of surface waters. In order that these models be as useful as possible, **a better surface water chemistry data base must be compiled** which includes information on biota. Only with such a data base will it be possible to assess the extent and nature of the risk to the resource.

Steps should be taken, either within any continuing program or by external means, to provide for **periodic updating** of the **emission inventory** and the **world literature reviews**.

Finally, the **data already obtained comprise a major resource**. Personnel and time should be devoted to **maximizing the further reporting**, and thus utilization, of that body of information.

**11. PEER REVIEW by The Science Advisory Board (SAB), Acid Deposition Research Program (ADRP), Biophysics Research Program**

The Present and Potential Effects of Acidic and
Acidifying Air Pollutants on Alberta's Environment.
Critical Point I. 1988. Draft Final Report, Volumes I and II.
Submitted by the ADRP Biophysics Research Group
Kananaskis Centre for Environmental Research
The University of Calgary.

## GENERAL EVALUATION

Based on the information presented to us and the level of knowledge available, it is the unanimous consensus of the SAB that:

1. The research conducted by the Biophysics Research Group has met, to our satisfaction, the mandate of the ADRP Members Committee.
2. The work conducted by the program scientists is of the highest quality, and they should be commended for their dedication and commitment.
3. We also commend the ADRP Members Committee for initiating and sponsoring this research.
4. The measurements made at Fortress Mountain and the resulting knowledge of background air quality will serve as a benchmark for the rest of Canada and the United States.
5. Concerning environmental effects, there are no presently observable or measurable regional-scale impacts in Alberta on crops, soils, or surface waters.
6. If only acidic and acidifying pollutants are considered, future regional impacts on crops are not credible, but adverse effects on unmanaged soils and surface waters are possible. If ozone is also considered jointly with sulphur and nitrogen oxides, then future adverse effects on crops and other plant life are also possible.
7. The SAB recommends continuation of research by the Biophysical Research Group, ADRP, beyond Critical Point I. Models indicate: those areas where pollutant concentrations reach maximum values; those areas most susceptible to adverse effects; and those media in which these effects are most likely to be manifested. None of these models, however, were developed for, nor validated in, this area or climatic regime. A close coupling of field examination, ambient monitoring, and laboratory studies should reveal the pertinence of the assumptions underlying the models to the environment of Alberta. This will also permit the necessary time for exploitation of the database already accumulated.

The SAB wishes also to express their gratitude to the ADRP Members Committee and the program scientists for allowing the Board Members a role in this important research.

## SPECIFIC EVALUATION AND RECOMMENDATIONS

### A. VEGETATION

BACKGROUND:

1. No regional-scale assessments of tree responses in Alberta were made prior to **Critical Point I**.
2. The alfalfa growth and $SO_2$ response models indicated that alfalfa yields might be lower than expected in the eastern portion of Emission Region 7.
3. Air monitoring results discussed in **Critical Point I**. findings suggest that ozone levels could have potentially adverse effects on forest and crop plants.
4. At the present time, data bases required for modelling are inadequate.

RECOMMENDATIONS:

1. Because modelling results in Emission Region 7 suggest possible decreased yields associated with $SO_2$, it is recommended that limited studies be conducted to determine the accuracy and validity of such modelling in terms of the suggested cause in this area only.
2. Predictive models are desirable for forest and crop plants exposed to ozone, sulphur dioxide, and nitrogen oxides following suitable injury threshold determinations made via controlled air pollutant exposures.

### B. SOILS

RECOMMENDATIONS

1. Because acid-sensitive soils have been identified in Alberta, it is recommended that wet and dry deposition monitoring be conducted in the vicinity of such soils to obtain data essential for assessing effects. In addition, the chemical and physical properties of such soils should be studied to provide information necessary to validate soil models.
2. Nutrient cycling and effects of temperature on the same, primarily nitrogen and sulphur, should be investigated on both acid-sensitive and non-sensitive soils to provide the basis for comparison of the parameters (e.g., $Q_{10}$, rate of nitrate and sulphate release) of nitrogen and sulphur cycling in these soils.

3. In forest soils, it is important that work be initiated to determine the forms and quantities of various organic acids produced in the litter layer with attention being placed on their contributions to the release and movement of aluminum, soil acidification, and changes in surface water chemistry.
4. The role of microorganisms in litter decomposition should be considered commensurate with studies mentioned above.
5. Models suitable for assessing acid impacts on forest soils should be developed and validated for the environment of Alberta.
6. The capacity of forest soils for sulphate adsorption should be studied, especially in highly acidic soils.

## C. SURFACE WATERS

### RECOMMENDATIONS

Because the modelling results for both the soils and surface water assessments indicate a potential for occurrences of acidification in sensitive areas of Alberta, we recommend that the following work be undertaken:

1. Develop a high quality surface water chemistry data-base including information on biota to permit more accurate assessment of the extent and nature of the resource at risk. (An exemplary model is the "Adirondacks Lake Survey Corporation" which represents a collaboration effort between the industry and government in New York State.)
2. Focus on forested areas and conduct integrated forest watershed/surface water effects studies in sensitive areas. Include studies of the potential effects of acidic episodes on the chemistry and biota of surface waters.
3. Examine the relationship among forest soil/surface water interactions and natural surface water acidification processes.

## D. AIR QUALITY

### RECOMMENDATIONS

1. Background and several additional rural monitoring sites should be established in the province of Alberta to measure ozone ($O_3$), sulphur dioxide ($SO_2$), nitrous acid ($HNO_2$), nitric acid ($HNO_3$), ammonia ($NH_3$), aerosol composition (e.g., elemental composition, nitrates, and sulphates), and rain chemistry to validate presently predicted future effects of industrial emissions on vegetation, soils, water resources, and air quality.

2. The enormous amount of air quality data, models, meteorology, emission inventory, and related information generated as part of ADRP should be processed and published in the peer reviewed literature. In order to prepare these publications, resources beyond the termination date of the ADRP need to be provided to satisfy this recommendation.

3. The wet and dry deposition flux measurements provided baseline data that quantify the types and amounts of acid deposition, as well as the relative magnitudes of wet and dry fluxes. These data are of the highest quality, and they set the state of the art in deposition in North America. The dry flux measurements are still of higher uncertainty than those for the more easily measured wet flux.

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